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

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1. Introduction
2. Chemo-responsive shape memory polymer nanocomposites
   2.1. Nanostructure/microstructure shape memory polymer composites
   2.2. Nanocellulose/shape memory polymer composites
   2.3. Carbon nanomaterials/shape memory polymer composites
   2.4. Bioactive glass nanoparticles/shape memory polymer composites
3. Electrically resistive Joule heating activated shape memory polymer nanocomposites
   3.1. Graphene filled shape memory polymer composites
   3.2. Carbon nanotube and nanofiber filled shape memory polymer composites
   3.3. Metal nanoparticles filled shape memory polymer composites
4. Light-activated shape memory polymer nanocomposites
   4.1. Nanogold/shape memory polymer composites
   4.2. Nanocarbon/shape memory polymer composites
5. Microwave heating triggered shape memory polymer nanocomposites
6. Magnetically sensitive shape memory polymer nanocomposites
7. Conclusions

Conflict of interest
Acknowledgements
References

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 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 free 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 [8]. 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

\[ \text{T}_{\text{g}} \]
on par with the diffusion of the water molecules into the bulk. Consequently, the water-induced shape recovery rate is limited by the diffusion of water molecules until equilibrium is met. These results indicated that SDS of the composite and water were decisive factors for the water-induced SME. Additionally, the shape recovery rate strongly depended on the ambient temperature. The shape recovery ratio of the SDS-ER in water at 35 °C was about 20 times faster than the specimen at 20 °C [6]. The elastic macromolecule fragments of the SDS-ER discretionarily tangled together before deformation with high entropy. After pre-deformation, the tangled molecular chain was in an orderly permutation, which was a metastable structure with low entropy [6,13]. According to thermodynamics, a system's entropy typically increases with increasing temperature as demonstrated in the shape change of the SDS-ER. SDS increased the spacing between the crosslinking net points. The crosslink density of polymer networks influences its $T_g$. The decreased $T_g$ was also attributed to the crosslink density reduction with increasing SDS content [6]. The $T_g$ of the composite can be tuned by its SDS content, since the 12 carbon chain of SDS disturbed the chain interactions in the epoxy-based SMP. Furthermore, the water molecules plasticize the polymeric composites, increasing flexibility of the chains in SMP composite and decreasing its $T_g$ [5]. Therefore, the water-induced shape recovery rate of the composites can be controlled by tuning the synergistic effect of water and heat [6]. Above all, the results suggest that chemical interaction and the PSE are important influences on the water-induced SME.

Rahman et al. reported the nanotube embedded membrane which was made of polyaniline nanotube embedded in nanoporous (polycarbonate) membrane and one end of the nanotube was attached to a surface deposited thin polyaniline layer [14]. The nanocomposite membrane kept rolled up in dry condition and gradually expanded with increasing humidity in sealed environment. It was worth reminding that the nanocomposite membrane actuation relied on the asymmetric absorption and desorption of water molecules. The open side faces of polymer nanotube efficiently absorbed water molecules and the surface deposited thin
polyaniline layer rapidly evaporated water molecules, in presence of humidity gradient (Fig. 3).

In addition, batch foaming, injection foaming and natural cellular material [15–17] also can be able to manufacture uniform porous structure solvent-driven SMP composite. The molecular chains of composites will be expanded or stretched to provide space for increasing the solvent molecules absorption rate, which benefits solvent-driven SME due to plasticization. Cellulose aerogel is an ultra-lightweight and highly porous material. Jiang and Hsieh explored a self-assembled cellulose nanofibril aerogels with ultralow density, superior porosity, super water absorption capacity, high crystallinity and water-induced shape memory property via cyclic freezing–thawing without chemical crosslinking, which could rapidly absorbed water at around 100 times their own weight without noticeable changes in the volume or shape [18]. These materials possess low density, high-volume expansion, and high thermal/electrical insulation, which have the potential applied value in the clothing, sporting gear, and biomedical industries.

2.2. Nanocellulose/shape memory polymer composites

Nanocellulose as hydrophilic bulking agent is one of the most abundant, biodegradable and renewable natural biopolymers, so it has attracted a great deal of interest and has been utilized as nanofiller in polymer nanocomposites. There are some researches that take advantage of nanocellulose to prepare water-induced shape memory nanocomposites [18–25].

In Fig. 4, Zhu et al. proposed characteristic microstructure details of the water-sensitive SME programming cellulose nanowhisker/thermoplastic polyurethane (CNW/TPU) [19]. The CNW/TPU softened in the wet state due to water molecules breaking the hydrogen bonds between the nanowhiskers, which could deform into temporary shape. And the subsequent drying at 75 °C, the shape was fixed by forming three-dimensional hydrogen-bonded network between the nanowhiskers without water molecules. In the recovery procedure, the wetting composite recovered its original shape with decoupling the nanowhiskers network. The reversible hydrogen bonding of the cellulose nanowhiskers is the key of this approach which provides the possible applications in breathable clothing and medical devices.

Biodegradable and biocompatible SMP nanocomposites are attractive to use as minimally invasive medical devices. Wu et al. provided an approach to prepare enzymatically degradable cellulose nanocrystals/biodegradable poly(glycerol sebacate urethane) nanocomposites with water-induced SME [20]. Dagnon et al. fabricated a poly(vinyl acetate) based water-responsive SMP nanocomposite with carboxylated cellulose nanocrystals (CNCs) of varying charge densities via partial functionalization using different equivalent propylamine [21]. The results suggested that the charges on the CNCs might enhance water diffusion through the nanocomposite without adversely affecting the modulus of either the stiff or soft state. The nanocomposite membrane is able to offer a way to enhance the water diffusion rate without significantly impacting its mechanical properties due to changing the charge density of the CNCs in the nanocomposite.

2.3. Carbon nanomaterials/shape memory polymer composites

As two-dimensional nanomaterial, graphene oxide (GO) is a compound of carbon, oxygen, and hydrogen in variable ratios with plenty oxygenated functional groups [26,27], which is easy to disperse well among polymer in the molecule level through forming strong hydrogen bonding interaction between components [28]. Qi et al. prepared a graphene oxide reinforced polyvinyl alcohol (PVA/GO) nanocomposites. In Fig. 5, shape memory properties of PVA/GO nanocomposites increased with forming additional physical cross-linked points between GO sheets and a layer PVA of GO surface in the composite. The hydroxyl groups of hydrophilic PVA exhibited high affinity with water molecules which could weaken the primary hydrogen bonding of the PVA/GO nanocomposites [29]. The combined effects of the plasticizing effect and the competitive hydrogen bonding are the two main reasons for the water-induced shape recovery of PVA/GO nanocomposites. Besides that, carbon nanotubes (CNTs) are also effective reinforcing filler [30–32] for enhancing shape recovery force and speed due to their excellent mechanical properties as well as high thermal conductivity coefficient [33].

Traditionally, the researches of solvent-induced [34] and moisture-sensitive [35] SMP focus on polyurethane [36–39] and hydrogel [40–44] based SMP. Meanwhile, there are some effective theoretical approaches such as phenomenological approach
Fig. 4. Proposed rapidly switchable water-sensitive shape-memory mechanism for the cellulose nanowhisker/thermoplastic polyurethane comprising a cellulose nanowhisker percolation network in an elastomeric matrix. Reproduced from Ref.[19] with permission from the Royal Society of Chemistry 2012.

[45,46] and constitutive model [47] about studying the constitutive relations and shape memory mechanisms of the chemo-responsive SME. The polymer network can gradually imbibe the certain solvent molecules causing change in the volume and shape, until reaching equilibrium condition in the particular environment. However, these solvent-induced SMP in general exhibit lower strength and stiffness, which limits their applications. It is concluded that the chemical and physical crosslinking of SMP nanocomposites overcome the weakness of thermal stability and exhibit excellent SME.

2.4. Bioactive glass nanoparticles/shape memory polymer composites

Bioactive glass nanoparticles (BG-NPs) have ability to induce apatite precipitation upon immersion in simulated body fluid [48], which can be used in tissue engineering or other biomedical applications. Correia et al. synthesized chitosan/bioactive glass nanoparticles (CHT/BG-NPs) scaffolds which combined the shape memory properties of chitosan and the biomineralization ability of BG-NPs for application as shape memory bone implantable materials [49,50]. Chitosan (CHT) is a linear polysaccharide which is one of the most widespread used natural polymers in self-healing and biomedical application due to its unique properties, such as antibacterial activity, wound healing property, biocompatibility and biodegradability [51]. It is also worth noting that CHT can be triggered by hydration and recover the permanent shape at room temperature attributed to its hydrophilicity and pore [52,53]. In their study, BG-NPs as reinforcing fillers increased the stiffness of the CHT/BG-NPs scaffolds. The temporary shape of the scaffolds was fixed by ethanol dehydration. The combined effect of solvent and non-solvent in miscible liquid pairs was used to control the swelling ratio of polymer networks. Water molecules disrupted intermolecular hydrogen bonds allowing large-scale segmental mobility upon the occurrence of \( T_g \), temperature to recover the original shape of pre-deformed scaffolds. Furthermore, water content could control the molecular mobility of the polymeric structure. Therefore, the water was used to induce shape recovery by hydration and ethanol was used as a non-solvent to control the CHT/BG-NPs scaffolds swelling capability.

Fig. 6A showed that the previously deformed CHT/BG-NPs scaffold was placed in the empty space of a fresh pig femur with size between the permanent and temporary shape of the scaffold. Fig. 6B showed that the recovered scaffold fitted perfectly the geometrical contour of bone defect with good mechanical fixation attributed to press-fitting effect. The scaffold combines biodegradability and shape memory capability for application in controlled drug release and minimally invasive surgery.

3. Electrically resistive Joule heating activated shape memory polymer nanocomposites

The electrically driven method is more precise, convenient, and efficient than heat-triggered actuation. The electrical current passage of SMP nanocomposites with sufficient conductivity is able to generate resistive heating by electrical triggering. However, SMP is typically good electrical insulator, so it is important to establish sufficient electrical conductivity of SMP nanocomposite without adversely influencing the shape memory performance. Electrically resistive Joule heating activated SMP nanocomposites have promising applications involving actively moving polymers with significant macroscopic deformation in a predefined manner. These nanocomposites can greatly improve the performance of the SMP and expand their potential applications through incorporation of electrically driven SMP composites utilizing graphene, CNTs, carbon nanoparticles, carbon nanofibers, and metal nanoparticles as conducting filler.

3.1. Graphene filled shape memory polymer composites

Graphene is a unique two-dimensional structure carbon materials possessing excellent electrical, thermal and mechanical
properties [54,55]. Based on the electrical conductivity and high modulus of the reduced graphene oxide paper (RGOP), Wang et al. used RGOP as functional layer to manufacture the reduced graphene oxide paper/epoxy-based shape memory composite which exhibited excellent electric-induced SME [56]. RGOP acted as conductive layer to generate resistive Joule heating and transmit the heat to the polymer stimulating shape recovery of the composite. The results showed that the storage modulus increased for compositing with RGOP, which was supported by micro/nano-mechanical tests [56]. It was worth noting that shape recovery rate of the composites approximated 100% only taking 5 s under 6 V which was much lower voltage than previous researches [57–64]. The temperature increased 74.81 °C comparing with the initial temperature at 1 s to activate the actuator. Subsequently, the actuator became more thorough. In Fig. 7, the uniform surface temperature distribution indicated the composite possessed adequate electric heating performance. Furthermore, the shape recovery rate of the composites strongly depended on the applied voltage which was decreased with increasing voltage. The electrical actuation shape memory property of the composite can be controlled by tuning the synergistic effect of component ratio and applied voltage. This work suggests feasible design principles of electrically driven SMP composites.

Valentini et al. reported a transferring method which was able to transfer graphene nanoplatelets (GNPs) layer from the glossy surface to polyurethane (PU) copolymer film [57]. Applying a constant voltage of 10 V, the sample recovered the original shape at least 20 s [57]. The results shown that the GNPs not only improved mechanical properties of PU film, but

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**Fig. 5.** (a) Illustration of hydrogen bonding interaction among PVA, GO and water; (b) schematic representation of the shape-memory PVA/GO materials actuated by water. Reproduced from Ref. [29] with permission from the Royal Society of Chemistry 2013.
3. Carbon nanotube and nanofiber filled shape memory polymer composites

The CNT possesses fascinating properties such as high thermal and electrical conductivity which encourages to utilizing them as functional filler in polymer nanocomposites [65–67]. In the work of Wang et al., they developed a chemically cross-linked polycyclooctene (PCO)-multiwalled carbon nanotubes (MWCNTs)/polyethylene SMP nanocomposites with co-continuous structure and selective distribution of fillers in PCO phase [59]. The MWCNT was selectively distributed in the composite which could observably reduce the fillers content for the same conductivity. The nanocomposites completely recovered with 150 V in 2 min [59]. Alam et al. prepared an electroactive SMP nanocomposite with epoxidized linseed oil plasticized polyactic acid and MWCNTs. The 3 wt% MWCNTs-reinforced nanocomposite system finished 95% shape recovery within 45 s at 40 DC voltages [60]. Sahoo et al. reported the polyurethane/multi-walled carbon nanotubes (PU/MWNTs) composites which were added MWNTs and polypyrrole (PPy) to enhance the conductivity of the electroactive shape memory composites. PU containing 2.5% PPy-coated MWNTs showed better mechanical, thermal, and electric properties, which finished 90–96% shape recovery within 20 s at 25 V [61].

The electrical alignment is a most convenient and efficient approach to align electronic polarized single CNT along the direction of the electric field [68,69]. The CNT tends to assemble into conductive chains along the external electric field with electrode distance in micrometer or even nanometer ranges [70]. The small distance between two CNTs leads to the strong Coulombic force between oppositely charged ends forming the local attraction field, so that CNTs attract each other to assemble into conductive chains. In Yu et al. study, the CNT was electrically induced into aligned chains in a SMP/carbon black (CB) composite which would act as long-distance conductive channels [62]. The viscosity of the liquid polymer is the key influence factor for the dipole moment

also generated resistive Joule heating transferred to the PU substrate.

3.2. Carbon nanotube and nanofiber filled shape memory polymer composites

Fig. 6. (A) Illustration of CHT/BG-NPs recovery in a defect produced in a pig femur bone. (B) Representative images of tree orthogonal Micro CT slices (horizontal, frontal and vertical projections) of a CHT/BG-NPs scaffold after recovery in the bone defect. Arrows indicate the site of the filled bone defect. Reproduced from Ref. [49] with permission from Elsevier 2015.
of CNTs [71]. In order to reduce viscosity of the shape memory resin, a dimethylformamide solution 50 vol% was added into the SMP matrix, which would be vaporized during the curing process. The electrical resistivity of the composite with well chained CNTs was reduced for more than 100 times comparing to the same amount randomly filled CNTs one. In Fig. 8, the fabricated conductive SMP/CB/CNT could full recover within 75 s at 25 V direct current electric voltages due to the remarkable reduction in electrical resistivity [62].

In our other work, self-assembled carbon nanofiber (CNF) and boron nitride (BN) functionally graded nanopaper of electrical actuation shape memory nanocomposites was enabled to actuate by electrically resistive Joule heating [63]. Here, BN was utilized to improve heat transfer and electric-activated shape recovery of the nanocomposite. The nanocomposite constituted with 0.16 g nanopaper (0.08 g CNF and 0.08 g BN) had the 96.7% recovery ratio at voltage of 4.8 V in 80 s with the maximum temperature reaching approximately 167.49 °C [63].

3.3. Metal nanoparticles filled shape memory polymer composites

Notably, some attempts have been made to inductively form conductive chains with applying magnetic field during curing the nanocomposite. For instance, Li et al. developed a type of chemically cross-linked poly(3-caprolactone) based SMP composite with Fe3O4 nanoparticles decorated multiwalled carbon nanotubes (Fe3O4@MWCNTs) as a magnetism and electricity responsive source [64].

The nanocomposite exhibited multistage stimulus SME in alternating magnetic field, electric field, and temperature field, respectively. In this study, the average size of Fe3O4 magnetic nanoparticles was about 20 nm which was suitable for keeping excellent magnetic responsive performance. The most outside surface of the carboxyl-modified MWCNT was covered by Fe3O4 nanoparticles. On the one hand, the Fe3O4 layers made a great contribution to the magnetic properties. On the other hand, the MWCNT without loaded Fe3O4 contributed to the good electric
properties. In Fig. 9, shape memory recovery processes of the composites were induced by hot water with different temperatures, an alternating magnetic field with frequency of 20 kHz, and an electric field with applied voltage of 60 V, respectively [64]. Osteoblasts were cultured to evaluate the cytotoxicity of the composite. The results demonstrated that it had good biocompatibility, and potentially application in biomaterials [72].

4. Light-activated shape memory polymer nanocomposites

The light-activated SMP is unique attributing to its unparalleled remote activation and spatial control without invading the material, local effect without compromising the property of the rest material, and easy switching on-off feature. It usually employs the photo-reversible covalent cross-links, which is photo-responsive cinnamic acid type molecules as switches under appropriate light radiation [2]. Commonly, functional fillers of light-activated SMP nanocomposites absorb light energy and transform light energy into heat to perform SME [73–79].

4.1. Nanogold/shape memory polymer composites

Gold nanoparticles (AuNPs) and nanorods (AuNRs) attract more attention for absorbing light at their surface plasmon resonance (SPR) wavelengths and thus generating heat release [80–83]. In Zhang and Zhao study, they described a rational design strategy that achieved the chemically cross-linking crystalline polymer with AuNPs to exhibit both light-activated SME and fast optical healing capability based on the same localized heating effect arising from the SPR of AuNPs [82]. Herein, the stimuli-healable polymer benefited to prolonging the service lifetime and reducing the cost due to repair damage (crack or fracture) with external stimulus. However, the difficulty of constructing this material is the structural incompatibility between two polymers. The SMP usually possesses permanent network structure which restricts chain motion with a high modulus [1], but the SMP requires the high chain mobility and inter diffusion [78,84–92]. This material design was based on that photothermally induced melting followed by recrystallization to optically heal (weld) thermoplastic crystalline polymers [80,81,93–95] and the photothermal effect for light-activated SME [73,96–98]. As shown in Fig. 10, poly(ethylene oxide) (PEO20K) of both chain ends terminated with an acrylate moiety was mixed with functionalized AuNPs, ammonium persulfate (APS), and N,N,N’,N’-tetramethylethylenediamine (TMDEA) before cross-linking reaction, which subsequently was cured at room temperature and 60 °C. The results indicated that a lower molecular weight PEO increased the network density leading to reduce the PEO crystallinity and difficulty achieve the optical healing effect. Moreover, AuNPs were well dispersed in the cross-linked PEO matrix displaying a SPR absorption band at ∼530 nm [82]. The nanocomposite showed selectivity locally light-activated SEM in laser irradiation (λ = 532 nm, 7 W/cm²) for photoinduced heating of the polymer to T > Tm of PEO [82]. Shape recovery took place quickly and only in the selected region with sufficient power laser irradiation. And then the process stopped almost immediately for fast cooling of the material to T < Tm once the laser turned off. Control tests found that the samples without AuNPs could not recover the original shape under the same conditions, which suggested that any possible heating effect resulting from laser exposure was not enough to activate the thermal phase transition of shape recovery. Same as the SME, the crosslinked PEO containing no AuNPs could not achieve optical healing effect under otherwise equal conditions. Surprisingly, the optical healing of the AuNPs composite was effective, but the bulk heating could not lead to heal the crack. The same phenomenon was also observed in a crosslinked polyethylene [99]. With heating the whole composite, the thermal expansion occurred freely throughout the sample leading to outward expansion which prevented intimate contact, chains interdiffusion, and interlocked chain recrystallization of fracture surfaces. By contrast, when the crack of the composite was selectively exposed in laser beam, the photo-induced heating occurred locally resulting in confined-thermal inward expansion without outward expansion. The localized expansion could generate hoop stress to push the fracture surfaces into contact benefiting chain interdiffusion and recrystallization for sewing the crack without external force.
Zhang et al. reported a unique photo-thermal effect which based on chemically cross-linked poly(ethylene oxide) with small amount (0.5 wt%) of AuNPs [100]. The controlled SPR absorption of AuNPs allowed for forming a temperature gradient in the polymer of temporary shape with anisotropic polymer chain relaxation and strain energy release. The pre-tensile nanocomposite bent with a small angle in the laser, when the AuNPs of near surface layer absorbed light first and released heat with chain relaxation of orientated chains in the upper surface. The polymer chain relaxation occurred in deeper and deeper layers with heating downward along the thickness direction under continuous laser radiation. The strategy could make it possible to use a laser to release of strain energy for creating complex shape transformations and controlling delicate mechanical work of SMP nanocomposites which were inaccessible usually or cannot be matched by direct heating or other stimuli. They also demonstrated that light polarization could be used to control photothermal effect-based gold nanorods (AuNRs)/poly(vinyl alcohol) (PVA) film in which anisotropic AuNRs was aligned in the nanocomposite [101]. The temperature rise could be tuned by different polarized light keeping all other conditions unchanged. The results indicated that AuNRs had excellent orientation along the stretching direction of the film. The polarization parallel with the stretching direction designated as 0° polarization angel. Longitudinal absorption was observed while the transverse absorption was absent. And yet the polarized light was set to be perpendicular with the stretching direction designated as 90° polarization angle. The longitudinal absorption disappeared, while only the transverse absorption was visible [101]. The key of the method is to choose low $T_m$ for semicrystalline or $T_g$ for amorphous SMP matrix for constructing orientation photoactive species/SMP film which has possibility of using the polarized light to control the shape recovery process.

Zheng et al. reported a light induced SMP micropillar (10 mm in diameter, 40 mm in height, and 20 mm in pillar-to-pillar distance) in a hexagonal array containing 0.1–0.2 mol% AuNRs via replica molding from a poly(dimethylsiloxane) (PDMS) mold [102]. The results suggested transmittance in the visible wavelength and water contact angle of the composite could be regulated by tuning bent and straight of SMP micropillar array. The SMP micropillar array film has potential application in light-guided smart windows or light-tracking solar panels.

4.2. Nanocarbon/shape memory polymer composite

Infrared light possesses wide emission spectra and unique heating effect in a noncontact manner which might be a good alternative to induced-heating. Lu et al. found that a unique synergistic effect of CNTs and boron nitride which could facilitate the thermally conductive and accelerate the infrared light induced shape recovery behavior of the SMP nanocomposites [103]. The CNCs were modified with benzophenone group which had highly photoactive and easily formed covalent bonds with each other and/or with surrounding macromolecules in polymer matrix.

Biyani et al. reported a light-stimulated mechanically switchable nanocomposite which was fabricated by incorporating benzophenone-derivatized cellulose nanocrystals (Bp-CNCs) into rubbery ethylene oxide/epichlorohydrin copolymer (EO-EPI) matrix [104]. They used a straightforward method to functionalize CNCs with benzophenone (Bp). The Bp-CNCs could mitigate wettability of the composite in humid environments. The EO-EPI/Bp-CNCs nanocomposite exhibited multi-responsive and mechanical switching characteristics. As mentioned earlier [18–24], the hydrogen-bonded of CNCs network in these materials led them to exhibit water-responsive SME. Bp with reliable photoactive moiety was usually used as photopatterning and photoinitiator [105–110]. In excited states, the UV light-activation Bp preferentially consumed nearby C–H bonds to form a new C–C bond [111,112]. In Fig. 11, Bp-CNCs as light-activated mechanically adaptive materials could be triggered to form bonds among CNCs as well as between CNCs and the surrounding rubbery EO-EPI matrix in light exposure [104]. When the Bp absorbed photon, one electron promoted from the nonbonding $n$ orbital to an antibonding $\pi^*$ orbital of its carbonyl group. This $n$–$\pi^*$ transition yielded a biradicaloid triplet state where the electron-deficient oxygen $n$-orbital was electrophilic [113,114]. Therefore, it was presumably preferential that the covalent bonds between Bp-CNCs eventually developed Bp-CNCs networks. It is worthwhile to note that this approach can be easily extended to use Bp-CNCs with more matrices.

The light-responsive SMP as a photomechanical material has the capability to directly transfer light energy into mechanical work played an important role in smart actuators, artificial muscles, and microelectromechanical systems [116–118]. Yu et al. fabricated a photoresponsive flexible graphene oxide/polymer nanocomposite film using a facile solution casting method [115]. The nanocomposite film displayed fast, stable, and reversible photomechanical behavior attributed to the photothermal effect of graphene oxide and the SME of the unique programming polymer matrix. They imitated the wobbly man structure for achieving light-powered tumbler movement of the film. The reversible tumbler movement was only triggered and maintained by visible light without external force, which was attributed to the incorporation between the photothermal effect of GO and the SME of the unique programming polymer matrix. They compared to CNTs and AuNPs, GO has better visible light absorption and is easier uniform dispersed in matrix. Furthermore, GO with unique photothermal property and high thermal conductivity would benefit photomechanical properties of the fabricated actuators [119]. Currently, the SMP composites could exhibit complex shape transitions utilized the shape programming process. In this study, the
nanocomposite film was programmed from a flat square to a cylinder shape with \( F = 0.6 \) to imitate the nondownable doll. The factor \( F \) was used to quantitatively characterize the bending degree of the film as given by Eq. (1) [115]:

\[
F = \frac{L_0 - L}{L_0}
\] (1)

Here \( L_0 \) and \( L \) were the linear length of the nanocomposite film before and after the shape programming process, respectively [115]. As expected, the nanocomposite film started the oscillation cycle with frequency of 0.5 Hz in visible light irradiation (450 nm, 54 mW/cm\(^2\)). In the initial state, the film \( (F = 0.6) \) was in an equilibrium state under the gravity and the bracing force with equal magnitude in opposite directions. During the unfolding process, the equilibrium state of the film was unavoidable broken attributed to asymmetric shape of the unfolded film \( (F = 0.5) \) under visible-light irradiation. As a result, the film rocked to the right with its gravity center simultaneously shifting to the right side. When it reached the extreme right position, a left-rotation force moment was produced to enable the film recovering to its initial position [115]. Then, the film would rock to the extreme left with its gravity center simultaneously shifting to the right side for the motion inertia. In this way, one tumbler cycle movement was achieved, when the action line of gravity and bracing force exhibited the displacement leading to drive the film rotating toward the reverse side. The continuous tumbler movement of the nanocomposite film could be kept exerting visible-light irradiation as an external stimulation in the whole process.

The PVDF-HFP copolymer had three crystal phases of CrPs\(_1\) \( (T_1 = 40.4 \, ^\circ\text{C}) \) and CrPs\(_2\) \( (T_2 = 75.5 \, ^\circ\text{C}) \) as switchable domains, while CrPs\(_3\) \( (T_3 = 131.2 \, ^\circ\text{C}) \) acted as the physical crosslinked networks determining the permanent shape. In Fig. 12A, the characteristic melting points of PVDF-HFP were not obviously influenced by the incorporation of GO [115]. GO could effectively absorb visible light and transfer it into thermal energy heating the nanocomposite film from 28 \( ^\circ\text{C} \) to 48 \( ^\circ\text{C} \), which was higher than \( T_1 \), but lower than \( T_2 \), leading to the shape change from shape B to shape C (Fig. 12B). It was important that the crystal phase CrPs\(_2\) remained and acted as an internal skeleton to promise the melted crystal phase CrPs\(_1\) recovering its original state in the recrystallization process [120]. Therefore, shape C would recover to shape B with removing visible light. If the crystal phases CrPs\(_1\) and CrPs\(_2\) of the nanocomposite film were melting, the film would directly change from shape B to shape A with the temperature rapidly increased higher than \( T_2 \), but lower than \( T_3 \). Thus, the nanocomposite film could not recover to shape B or shape C exhibiting reversible photomechanical behavior, although the temperature decreased to 28 \( ^\circ\text{C} \) [115]. This work would have a significant impact on actuation devices such as soft robots [121], inchworm walkers [122], motors [123], and smart curtains designed based on movement modes of photomechanical materials.

5. Microwave heating triggered shape memory polymer nanocomposites

Microwave is an electromagnetic energy ranging from approximately 1–100 GHz in frequency. In comparison with other electromagnetic waves, microwave possesses better penetrability with the low attenuation degree during transportation. Therefore, microwave can be used as practical remote controllable, environmentally friendly, highly efficient, uniform, and rapid actuation method for SMP without temperature gradient, hysteresis effect, considerable energy loss, and preheating, which heats materials in molecular level and meets the high requirements of uniform heating. Microwave heating triggered SMP nanocomposites offer an opportunity for potential applications in the biomedical treatments such as tissue engineering and regenerative medicine. According to the interaction with microwave, the materials may be divided into three groups, which are absorbers, insulators and conductors.
The absorbing microwave materials are called dielectrics. There are two basic properties of the materials to govern its interaction with electromagnetic fields in the area of microwave heating. One is the real part of dielectric (dielectric constant, \( \varepsilon' \)), which measures the ability of storing electrical potential energy. The other is the imaginary part of dielectric (dielectric loss factor, \( \varepsilon'' \)), which measures the efficiency of transforming electromagnetic energy into thermal energy. The absorbed microwave energy is transferred into thermal energy through molecular friction and collisions [124–126].

CNTs, silicon carbide (SiC), ferroelectric nanoparticles, and water molecules usually used as microwave energy absorbers to construct microwave-induced SMP nanocomposites [127–129]. Currently, the interaction mechanism between CNT and microwave was usually attributed to its impurities [130–133], generation of gas plasma [134], and dipolar polarization [135]. There are no significant temperature gradients within the CNT/SMP composites, so no residual stress generated during the microwave actuation of the composites. In the study of Yu et al., the CNT with superb electrical, mechanical, thermal, and strong microwave absorbing properties used as microwave energy absorber in CNT/styrene-based SMP composites [127]. The CNT in the polymer matrix as the internal thermal sources transferred the absorbed electromagnetic energy into heating to induce shape recovery of the SMP composites. The results indicated that the CNT/SMP composites could successfully be induced by microwave radiation frequency of 2.45 GHz (40 W) and 5 wt% CNT of the SMP composites could absorb 99.84% of the microwave energy under microwave radiation frequency of 40 GHz [127]. The microwave absorption ratio of the CNT/SMP composites increased along with increasing the CNT content or the microwave frequency. In Fig. 13(a), the CNT/SMP part began to recover its original shape and constricted in length with heating above the \( T_g \) temperature under microwave radiation, but the pure SMP part could not be heated which generated an inhomogeneous strain in the composite leading to the specimen wrap up. As shown in Fig. 13(b), the bending angle of the specimen was approximately 50° in 30 s under microwave irradiation, subsequently decreased by further exposure in the microwave field due to thermal conduction from the composite part to the pure SMP part [127]. The selective heating effect of nonuniform SMP in the microwave field can be used in the rapid remote controllable actuation switch or device.

As a functional material, SiC has many good properties, such as strong microwave absorbing, low thermal expansion coefficient, good chemical stability, and high temperature stability [124,136,137]. As mentioned above, SiC can strongly absorb microwave heated rapidly due to its dielectric loss factor. Du et al. prepared silicon carbide/poly(vinyl alcohol) based microwave heating triggered SMP composites, in which SiC molecules as the dielectric exhibited a dipole movement under the alternating electric field to generate friction heat for increasing chain segments flexibility and subsequently resulting to the polymer chains recover its original stress-free state at a molecular level [129]. Herein, microwave oven generally operated at a frequency of 2.45 GHz as an alternating electric field for heating. Hydrophilic modification of SiC had been done with silane coupling agent 3-triethoxysilylpropylamine to improve its dispersion in water and the compatibility in PVA matrix. The SMP composites had good thermal stability, mechanical properties, and microwave-induced SME, which recovered original shape within 1 min under 600 W microwaves.

The low viscosity, high solubility, high reactivity, and good compatibility of SMP are able to gain through designing novel molecular architecture with appropriate hard and soft domains. Kalita and Karak developed an in situ polymerization technique for the synthesis of microwave actuated hyperbranched polyurethane/Fe\(_3\)O\(_4\) nanoparticles decorated multiwalled carbon nanotubes (Fe\(_3\)O\(_4\)-MWCNTs) thermosetting shape memory nanocomposites [138]. Fe\(_3\)O\(_4\) nanoparticles decorated MWCNTs had not only increasing dispersion but also absorbing microwave characteristics [139]. In this case, the saturation magnetization value of Fe\(_3\)O\(_4\)-MWCNT was 0.23 emu/g and the tensile strength, scratch hardness, thermal stability, and shape memory properties of diglycidyl ether of bisphenol-A epoxy-based thermosetting nanocomposites were improved by increasing Fe\(_3\)O\(_4\)-MWCNT in the nanocomposite [138]. The cross-linking reactions among the –OH–C=O of Fe\(_3\)O\(_4\)-MWCNTs, epoxy/hydroxyl groups of the epoxy resin, and free–OH groups of the hyperbranched polyurethane led to restrict molecular chains movement and slippage, forming the three-dimensional network structures and increasing cross-linking density of the nanocomposite [138]. Based on the dose-dependent shape memory behavior, the nanocomposite can be tuned as the requirement. This nanocomposite is a noncontact microwave-induced shape memory material with good shape fixity and shape recovery ability.

6. Magnetically sensitive shape memory polymer nanocomposites

The coherent integration of inorganic nanoparticles in polymer matrices can improve the shape memory and structural properties of SMP composites. Magnetic nanoparticles have remarkable versatility, such as hyperthermia therapy [140,141], data storage [142,143], and microfluidics [144]. The magnetic properties of metal oxides such as Fe\(_3\)O\(_4\) with sub-100 nm dimensions are thoroughly different from those of the corresponding bulk materials [145,146]. When the magnetic particle size falls below a critical limit, the magnetic nanoparticles exhibit super-paramagnetic [147]. Due to the features, the magnetic nanoparticles as inductive heaters are considered to fabricate magnetically sensitive shape-memory polymer nanocomposites [148–150].

By adjusting the parameters of alternating magnetic field, the magnetically sensitive Fe\(_3\)O\(_4\)/SMP nanocomposite could recover their original shapes. Bai et al. used super-paramagnetic iron oxide nanoparticles (SPIONs) as macromolecular network crosslinking points and magnetic-inductive heating elements to construct norborne-based magnetically sensitive nanocomposites with ring-opening metathesis polymerization (ROMP) [151]. Traditional approach physically incorporated the iron oxide nanoparticles into the polymer matrix. In this work, the complexation of carboxylate...
moeities on Fe₃O₄ surface was strong enough to disperse well and form appropriately strong networks via specific non-covalent interactions. The nanocomposite exhibited good shape memory performance in an alternating magnetic field of H = 6.8 kA/m at a frequency f = 20 kHz [153]. Herein, radicals and free radical chains were caught by sodium oleate on Fe₃O₄ surface. And then rigid particles worked as obstacles to impede the proximity motion of radicals and free radical chains. This suggests that this modification method might be fitted to modify other SMP in principle. The nanocomposite was activated from their frozen temporary networks nanocomposites [157]. The surface-modified Fe₃O₄ nanoparticles could prevent nanoparticle aggregation and copolymerize with polynorbornene.

Yu et al. proposed a feasible and versatile method to prepare a biodegradable crosslinked poly(e-caprolactone) (c-PCL)/Fe₃O₄ nanocomposite which exhibited an good shape memory performance in an alternating magnetic field of H = 6.8 kA/m at a frequency f = 50 Hz [154]. The results indicated that the magnetically sensitive SMP nanocomposite was possible to be stimulated by an electromagnetic field of low frequency and low field strength.

Fe₃O₄ nanocrystals can be stabilized by interacting with the carboxylic acid groups of oleic acid on the surface [155,156]. Modified magnetite (Fe₃O₄) easily realizes well dispersion of the nanometer size range in polymer matrix. Yang et al. used a facile method to synthesize Fe₃O₄/poly(norbornene)-based alternating magnetic field triggered SMP nanocomposites [157]. The surface-modified Fe₃O₄ nanoparticles decreased the shape recovery induction time due to increase in thermal conductivity.

As previously mentioned, our group fabricated a SMP nanocomposite exhibited multistage stimulus SME in alternating magnetic field, electric field, and temperature field, respectively [64]. The nanocomposite exhibited good shape memory property in alternating magnetic field (f = 20 kHz, H = 6.8 kA/m). Cai et al. utilized in situ polymerization method to synthesize magnetically sensitive polyurethane composites which could be filled with high content of Fe₃O₄ nanoparticles due to the crosslinking of MWCNTs with polyurethane prepolymer [158]. Generally, a high content of magnetic nanoparticles in polymer matrix deteriorate its mechanical properties [159–161]. Herein, the nitric acid-MWCNTs were used as crosslinking agents to form network structures and improve the mechanical properties of the composites even with high content Fe₃O₄ nanoparticles. The shape recovery rate of the nanocomposite was over 95% in alternating magnetic field (f = 45 kHz, H = 29.7 kA/m) within 1 min. In a short time of the beginning, there was no observed shape change of composites in alternating magnetic field which was called magnetic field response time. At the later stage, the temperatures reached Tg and the composites recovered to their initial shape quickly.

Here Razzaq and Lendlein reported a poly(u-pentadecalactone) networks nanocomposites with three arm oligo(u-pentadecalactone) (OPDL), OPDL coated magnetite nanoparticles as multifunctional covalent netpoints at the nanoscale provided mechanical stability and magnetically sensitive shape memory performance [162]. They found that the performance of nanocomposites could be controlled by magnetite nanoparticles content according to their applicability which focused in the direction of mechanical strength or shape-memory actuation capability. A similar study of their group carried out detailed studies on electrospraying of a 1,1,1,3,3,3-hexafluoro-2-propanol solution containing a mixture of copolyetheresterurethane (PDC) and magnetic Fe₃O₄ nanoparticles to prepare magnetically sensitive polymer-based nanocomposite microparticles [163]. The electrospraying technique benefited for fabricating magneto-sensitive polymer-based nanocomposite more than entrapping process, suspension polymerization, emulsion polymerization, and dispersion polymerization, because it neither required high temperatures nor further drying step [164–166]. PDC was a copolyetheresterurethane composed of crystallizable oligo(p-dioxanone) as permanent netpoints and crystallizable oligo(e-caprolactone) as switching segments to trigger SME which were linked via a hexamethylene-1,6-diurethane unit [169].

7. Conclusions

The SMP nanocomposites can be optimized depending on application requirements to probe more interesting behaviors and study more challenging actuation problems. In this context, nanocellulose, CNTs, BG-NPs, graphene, carbon nanoparticles, AuNPs, Fe₃O₄ nanoparticles, and SiC nanoparticles have emerged as useful nanofillers. Besides conventional thermal stimulus, the chemo-responsive, electrically activated, light-activated, microwave triggered and magnetically sensitive SME can be used as potential driving methods to stimulate the SMP nanocomposites. Emphasis was placed on the design principle, fabrication, shape memory properties, and corresponding mechanisms of the SMP nanocomposites.

Researches on chemo-responsive SME generally agree that the plasticizing effect of solvent molecules can increase the flexibility of the hydrophilic SMP chains. In particular, the water-induced SMP have SME in water or physiological media at body temperature without heat. A water molecule is good plasticizer, which weaken hydrogen bonding between the polymer chains. Correspondingly, the chains attain greater mobility and increase in free volume, which decrease the Tg and stiffness. Adding functional nanomaterial and constructing nanostructure can largely improve chemo-responsive shape memory performance of SMP. The chemo-responsive SMP nanocomposites have the advantages of biological compatibility, facile processing, and good mechanical properties, which have the potential to give value in humidity sensors, underwater deployable structures, ultralow-power devices, breathable clothing, sporting gear, and biomedical industry. In some applications, electrical activation is a more convenient and efficient method than the external thermally triggered method. The research shows that higher content of conductive filler yields lower resistivity in the nanocomposites. However, it is difficult to
adequately disperse the filler in polymer matrices increasing filler content. The inhomogeneously dispersed fillers in nanocomposites not only cause non-uniform recovery with localized heating, but also lead to localized melting, and even present a fire hazard in extreme cases. These safety issues have been the primary obstacle in developing efficient electrically actuated shape memory nanocomposites. Comparing to other stimuli-driven methods, the light-driven method is a non-contact clean energy source that can be controlled remotely, instantly, and precisely. The photo-thermal effect of light-induced SMP nanocomposite not only possesses the appealing features of remote activation, spatial control, and switching capability, but also has the healing effect under certain conditions in precisely selected regions. Further developing light-induced SMP nanocomposites will have a significant impact on actuation devices such as soft robots, inchworm walkers, motors, and smart curtains based on movement modes of photomechanical materials. As other applicability of functionally graded SMP nanocomposites, its selective heating effect in the microwave field and magnetic field can be used in the rapid remote controllable actuation switch or device. It is expected to provide a new perspective and effective approach for designing novel SMP nanocomposites via understanding interrelationships between the design principle, fabrication, shape memory properties, and corresponding mechanisms.

Conflict of interest
Authors declare no competing financial interests.

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