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Review Article

Applications of Shape Memory Polymers in Kinetic Buildings

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Shape memory polymers (SMPs) have attracted significant attention from both industrial and academic researchers, due to their useful and fascinating functionality. One of the most common and studied external stimuli for SMPs is temperature; other stimuli include electric fields, light, magnetic fields, water, and irradiation. Solutions for SMPs have also been extensively studied in the past decade. In this research, we review, consolidate, and report the major efforts and findings documented in the SMP literature, according to different external stimuli. The corresponding mechanisms, constitutive models, and properties (i.e., mechanical, electrical, optical, shape, etc.) of the SMPs in response to different stimulus methods are then reviewed. Next, this research presents and categorizes up-to-date studies on the application of SMPs in dynamic building structures and components. Following this, we discuss the need for studying SMPs in terms of kinetic building applications, especially about building energy saving purposes, and review recent two-way SMPs and their potential for use in such applications. This review covers a number of current advances in SMPs, with a view towards applications in kinetic building engineering.

1. Introduction

Shape memory polymers (SMPs) are an emerging class of intelligent polymers that can change their shapes in predefined ways, in response to appropriate stimulation [1]. Vernon et al. fortuitously discovered "shape memory" in polymers in 1941 [2]. In the 1960s, the utilization of covalently crosslinked polyethylenes (PEs) in heat-shrinkable tubing and film became another important milestone in the development of SMPs [3–6]. Significant efforts began in the 1980s to find additional applications, and this trend has continued in recent years (particularly in Japan and the US) [5, 6]. Compared with shape memory alloys (SMAs), SMPs possess the advantages of high elastic deformation, low cost, low density, and potential biocompatibility and biodegradability [6]. They also have a wide range of tailorable application temperatures and tunable stiffnesses and are easily processed [5].

SMPs typically consist of crosslinked segments that determine the permanent shape and switching segments at transition temperatures that fix the temporary shape [7]. Figure 1 shows the three-dimensional structure of an SMP. In Figure 1, a network-like architecture can be seen resulting from crosslinked net points (the black dots); the switch segment (the grey cube) connects them entropically to form a given macroscopic shape [8]. The permanent shape of the SMP is determined either by physical or chemical crosslinks. Therefore, based on the nature of the crosslinks, conventional SMPs relying on thermal phase changes can be categorized into two types, those that are either chemically or physically crosslinked. According to the nature of the switching segments, SMPs can also be divided into those with either amorphous or crystalline switching segments [7–9].

Upon the reversibility of shape memory effect (SME), SMPs can also be classified into either one-way or two-way SMPs. "One-way" implies that the shape recovery is irreversible. That is, shape shifting during recovery can only proceed from a temporary to a permanent shape and not the reverse (Figure 2). "Two-way" means that the shape change is reversible; the initial and temporary shapes can be reversed with the appearance and termination of the stimulus. Thus, these two-way SMPs can achieve dual or even triple shape changes (Figures 2 and 3). Two-way SMPs have received considerable attention in recent years because of their ability to change shapes in response to the external stimuli to which they are exposed. Many researchers have proposed potential applications in areas such as artificial muscles, textiles, and actuators [10–12]. In Section 4, we will discuss two-way SMPs and their potentials in detail.

Based on the number of shapes involved in each shape memory cycle, SMPs can be classified as dual, triple, or multi-SMP [13]. A typical SMP is dual (i.e., one temporary shape transformed into a permanent shape). In contrast, triple-SMPs feature two temporary shapes (A and B in Figure 3) in addition to their permanent one (C in Figure 3). First, the temporary shape B must be programmed, followed by the temporary shape A. The appropriate stimulus transforms the second temporary shape into the first (A→B). Subsequently, a second trigger initiates the regeneration of the permanent shape C. A multi-SMP (shown in Figure 3) is able to memorize more than two temporary shapes and subsequently recover in a highly controllable manner [14–16].

One of the most common external stimuli for SMPs is temperature. Many athermal stimulation methods (including electric fields, light, magnetic fields, water, irradiation, and solutions) for SMPs have been studied in the past decade. Based on such methods, SMPs can be classified into temperature-responsive, electric-responsive, magnetic-responsive, photo-responsive, or solution-responsive triple- or multi-SMPs. The corresponding mechanisms and properties (such as mechanical, electrical, optical, shape, constitutive model) of different stimulation methods will be discussed in Section 2.

SMPs are widely used in areas such as biomedical devices, aerospace engineering, textiles, energy, bionics engineering, electrical engineering, the development of household products, and civil and architectural engineering. Many extensive reviews have been conducted and published by various groups. These reviews have covered general aspects of SMPs [15, 16], multifunctional SMPs [17], SMP composites [18, 19], SMP foam [15–19], SMP fibers [20–23], and SMP characterization. However, from the perspective of possible applications, much of the discussion in these review studies has revolved around applications in the biomedical [17, 24, 25] and aerospace engineering [18, 26–28] fields. Given the trend in recent studies of investigating applications in civil and architectural engineering, it is worth reviewing the major efforts and developments there.

SMPs have been fabricated and used for critical civil infrastructure. Li et al. proposed that SMPs be employed as sealants such as SMP-based sealants [29], asphalt-based liquid sealants, two-way shape-changing polymer sealants, rutting resistance asphalt concrete materials, and self-healing materials for damaged structures [30–32]. Two types of SMP-based smart sealants have been successfully applied in compression-sealed joints in concrete pavement [32]. Carbon fiber reinforced SMP composites have been analyzed with the potential for application as lightweight compactible structures [22]. SMPs have also been investigated with regards to their use in repairing fatigue-sensitive steel elements [20] and as structural components (beams, rods, plates etc.) for vibration control and remote sensing actuators [33, 34]. Section 3 of this paper provides a brief overview of these applications in built environments.

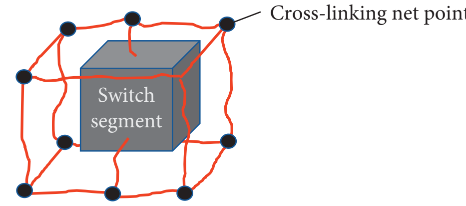

Figure 1: Modular architecture of an SMP.

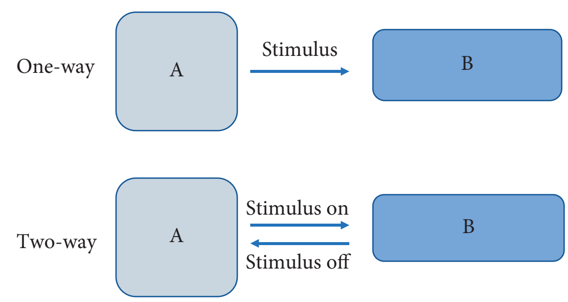

Figure 2: One-way and two-way SMPs.

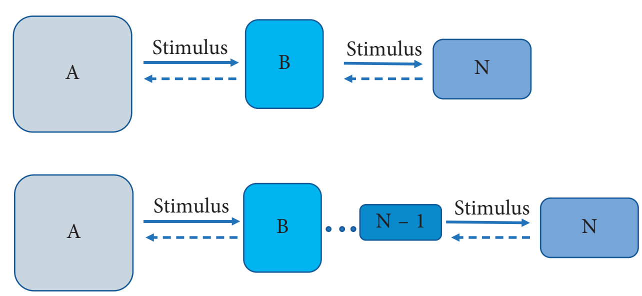

Figure 3: Triple- and multi-SMPs.

Nevertheless, two-way SMPs are more intelligent; they can sense environmental changes and respond to them in an optimal manner [35]. Applying two-way SMPs in built environments could offer real benefits, though there are still many difficulties with their proper engineering. Section 4 of this research concisely describes the mechanism of two-way SMPs, reviews certain popular areas of research, and lists particular challenges and opportunities related to their use in building and architecture applications.

2. Mechanisms of Different Stimulus-Responsive SMPs and Their Constitutive Models

2.1. Mechanisms of SMPs

2.1.1. Thermally Responsive SMPs. Most SMPs use heat as their stimulus [1]. These thermally responsive SMPs can be regarded as thermoplastic elastomers, in which there is a hard phase with a high glass transition temperature (T_g) and a second, switching phase, with an intermediate or melting temperature (T_m) that enables the thermally responsive behavior [36]. The temperature surpassing T_g (or T_m) is symbolized as T_{high} and the temperature being lower than T_g (or T_m) is symbolized as T_{low}. First, the SMPs can be processed into any shape desired as the permanent shape. Then, when the temperature is higher than T_g (or T_m) and reaching T_{high}, a temporary shape can be induced that can be then "frozen" by cooling the deformed state at the low temperature condition, T_{low}. Consequently, when heated above T_g (or T_m), the SMPs transform back to their permanent shape [13, 37]. The schematic drawing in Figure 4 shows this thermally responsive process.

Molecular switches and net points are two major molecular-level components of thermally responsive SMPs. Molecular switches are segments with a thermal transition at T_m that fixes the temporary shape by forming physical crosslinks. Net points that link these switching segments and determine the permanent shape of the polymer network can either be physical crosslinks through physical intermolecular interactions or chemical crosslinks through covalent bonds [36].

2.1.2. Photoresponsive SMPs. Photoresponsive SMPs can respond to light stimuli by undergoing reversible changes in their properties [37]. There are two main mechanisms that operate in light-induced SMPs: photochemical reactions leading to deformation and the employment of particles that convert light to heat [38, 39]. In photochemical reactions, intrinsically photoresponsive SMPs are produced by incorporating reversible photoreactive molecular switches when a special wavelength of light strikes them; this alters the structure of their crosslinked polymer networks. For example, Lendlein et al. showed that SMPs containing cinnamic groups can be deformed and fixed into predetermined shapes when exposed to alternating wavelengths ($\lambda > 260$ nm or $\lambda < 260$ nm) (Figure 5). The accumulation of structural alterations leads to an evolution of the polymer network and even subsequent macroscopic deformation. Consequently, photochemical SMEs are produced [38–41]. This stimulation is considered unrelated to any temperature changes. Therefore, it should be differentiated from the indirect actuation of thermally responsive SMPs [7]. Another photosensitive function is that molecular switches convert light to heat and then actuate thermally responsive SMPs [39]. Therefore, illumination with the radiant thermal energy of infrared light possessing a wide range of spectra ($500\sim4000\,\mathrm{cm}^{-1}$) can serve as a heat source for photoresponsive SMPs; these can then be applied with noncontact nonmediums [7, 39].

2.1.3. Electrically Responsive SMPs. Electrically responsive SMPs are also intrinsically of the thermally responsive type [18]. Thermally active SMPs are usually filled with electrically conductive ingredients that reach a certain level of electrical conductivity; this means that electricity, as a stimulus, enables their resistive actuation [7, 19]. Most SMPs have high levels of electrical and thermal resistance when the actuation is remotely controlled. They are heated via an electric current that passes through the conductive ingredient network within [18]. If the internal temperature is above the transition temperature, T_g, resulting in the permanent shape, then the SMP can be deformed into any shape. If the temperature is between T_g and T_m, a temporary shape can be induced and fixed by cooling the SMP to below T_m. Consequently, heating above the melting temperature, T_m, may trigger deformation recovery (Figure 4) [39]. Compared to the direct external heating method, the internal resistive joule heating method by electricity presents certain advantages, such as convenience, uniform heating, and remote controllability [18].

2.1.4. Magnetically Responsive SMPs. Similar to electrically responsive SMPs, thermally active SMPs embedded with magnetic particles are magnetically responsive. An alternating magnetic field (AMF) produces inductive heating, which triggers the recovery process. The temperature can be increased rapidly since the heat is normally generated inside the polymer itself [42, 43]. N e' el relaxation (eddy current losses), Brownian motion relaxation (rotational losses), and hysteresis losses are the three main heating mechanisms that operate AMFs. In the N e' el relaxation mechanism, in response to an externally applied AMF, a particle's magnetic dipole changes its orientation within the particle. The particle's magnetic moment of resisting this orientation produces heat, which is also counted in the particle's magnetism [43, 44]. In Brownian motion relaxation, in response to an externally applied AMF, a particle physically rotates to align with the magnetic field; the friction between the rotating particles (responding to the externally applied AMF) and the carrier fluid (due to the viscosity effect of resisting the particle rotation) results in heat [42–44]. In addition to relaxation losses in larger particles with a particle size > 20 nm, thermal energy can be stemmed from magnetic hysteresis losses [44]. Hysteresis describes a path that depends on the magnetic response of magnetic materials to an applied magnetic field. Hysteresis losses mainly occur in domain wall motion, such as when multidomain ferro- or ferrimagnetic particles are exposed to an AMF. The generated heat is proportional to the area of the hysteresis loop and frequency of the AMF [44]. Basically, the heating power associated with relaxation loss lower than that of the hysteresis losses [44].

2.1.5. Solution-Responsive SMPs. Solution-responsive SMPs present a significant decrease in the modulus during phase transition [45]. Water-driven actuation of SMPs was first discussed in 2005 by Huang [46]. In general, water or solvent molecules are able to infiltrate SMPs. Due to the plasticizing effect of water and solvent on SMPs and the increase in flexibility of macromolecules, the glass transition temperature, T_g, can be decreased after the addition of a small amount of water. When the glass transition temperature, T_g, approaches the ambient temperature, the recovery process of

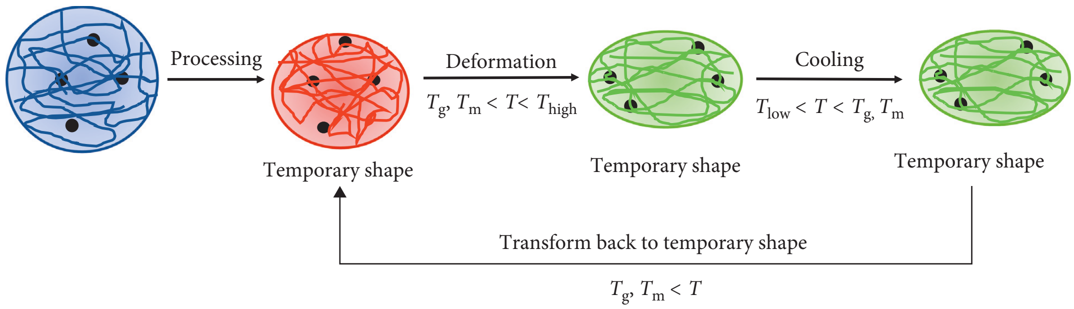

Figure 4: Thermomechanical cycle of thermally responsive shape memory polymers.

the water-induced SMP is triggered [18]. The interaction between macro- and micropolymeric molecule of the solution is the main mechanism behind this phenomenon. Three major reasons causing it are as follows: (1) the flexibility of the polymeric chains is magnified by the hydrogen bonding; (2) based on the continuum theories of rubber elasticity, the Mooney–Rivlin equation, and volume change refinement theory, the polymer modulus is destroyed due to the volume change in the polymer caused by the interaction; (3) the solution makes the polymer tender until T_g decreases to the temperature of the solution while T_g of the polymer is higher than the temperature of the solution or the ambient temperature. Consequently, the solution continues affecting the polymer's other aspects. T_g can decrease significantly and reach to the temperature of the solution because the micromolecular of the solution can weaken the elasticity modulus of the SMP. Therefore, the solution can trigger off the actuation of SMPs by means of reducing T_g of the material itself through immersing the SMPs into solution [45].

2.1.6. pH-Responsive SMPs. The pH-responsive SMPs have great potentials in medical applications. The physiological pH values vary in different sites of the body, which generally appears as a sharp gradient across biological systems on both the cellular and systemic levels in pathological states [47]. A pH-responsive SMP reported by Han et al. can be processed into a temporary shape at pH 11.5 and recover to its initial shape at pH 7 [48]. A pH-responsive SMP based on polyurethane and the pH-stimulated DNA hydrogels have been also proposed [47]. The mechanism of pH-responsive SMP is mainly based on the polymer swelling at different pH values of the environment. The pH value of the environment can act as a switch to control the shape memory without temperature variations. If the pH-responsive SMP prepared with some chemical materials, the key for realizing the SME is the hydrogen bond interaction. For example, the pH-responsive SMP prepared with functionalized cellulose nanocrystals (CNCs), the hydrogen bond interaction between the modified CNCs percolation network, and matrix materials decides the SME [49]; for the pH-responsive SMP synthesized by introducing pyridine rings into the backbone of polyurethane, the hydrogen bond interactions between the N atom of the pyridine ring and H–N of urethane in neutral or alkaline environments are the main contributory cause of the SME [47].

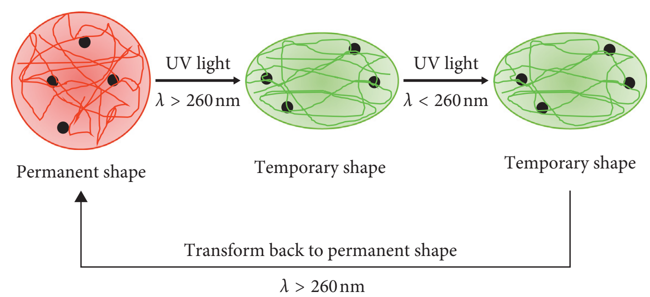

Figure 5: Schematic diagram of the molecular mechanism of photoresponsive SMPs.

2.2. Properties of SMPs

2.2.1. Constitutive Model of SMPs. The constitutive model describes the relationship between stress and strain. The most important component is the viscoelastic constitutive model. Tobushi et al. developed a linear viscoelastic constitutive model of SMPs, and further established a one-dimensional nonlinear constitutive model [47, 48]. Liu et al. advanced a three-dimensional linear constitutive model in two phases: the active phase at high temperatures and frozen phase at low temperatures [50]. Many researchers have developed different constitutive models of SMPs, based on Tobushi and Liu's research. The overall small-strain constitutive equations are shown as follows [50]:

$$\sigma = \frac{\varepsilon - \varepsilon_s - \int_{T_h}^{T} \alpha\, dT}{(\phi_f/E_i) + ((1-\phi_f)/E_e)} = E\left(\varepsilon - \varepsilon_s - \int_{T_h}^{T} \alpha\, dT\right), \quad (1)$$

where ε_s is the storable inelastic strain; ϕ_f is the frozen fraction; T_h is the temperature of the thermomechanical cycle starting; E is Young's modulus, $E = 1/((\phi_f/E_i) + ((1-\phi_f)/E_e))$; E_i is the modulus of the internal energetic deformation, usually $E_i = \text{constant}$; E_e is the modulus of the entropic deformation, usually $E_e = 3NkT$; N is the crosslink density; k is Boltzmann's constant ($k = 1.38 \times 10^{-23}$ Nm/K); α is the coefficient of thermal expansion, $\alpha = d\varepsilon_T/dT$; and ε_T is the thermal strain.

2.2.2. Shape Memory Effect. In order to explain the shape memory effect of SMPs, the shape fixity rate, R_f, and shape recovery rate, R_r, are normally used as characteristic factors. Shape fixing, or fixity, refers to the ability of an SMP to retain a temporary state, and thus store strain energy, by cooling below a transformation temperature. Shape fixing can be quantified by use of the measure:

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m(N)} \times 100\%. \quad (2)$$

The shape recovery rate can then be calculated as follows:

$$R_r(N) = \frac{\varepsilon_u(N) - \varepsilon_p(N)}{\varepsilon_u(N) - \varepsilon_p(N-1)}, \quad (3)$$

where $\varepsilon_u(N)$ represents the strain of cycle N after unloading, $\varepsilon_m(N)$ is the temporal strain of cycle N that is achieved after deformation, and R_f may depend on the shape memory cycle number, N. Also, $\varepsilon_p(N)$ and $\varepsilon_p(N-1)$ are the extensions in the tension-free states while expanding the sample in two subsequent cycles, N and $N-1$. At the molecular level, fixing can be designed in an SMP by organizing the constituent chains to crystallize or vitrify at a targeted temperature or by otherwise immobilizing the chains.

3. A Brief Survey of Applications of SMPs in Civil and Architectural Engineering

This section presents a brief review of recent trends in the field of SMPs, with a particular focus on their applications in civil and architectural engineering. Compared with previous reviews of the field [5, 9, 18, 19, 51], this review summarizes information on civil and architectural engineering applications. In general, SMPs are mainly used as sealants and self-healing materials, vibration control systems, and actuators or sensors for structural health monitors. In addition, potential applications as smart materials for built environments are outlined in Figure 6.

3.1. Sealants and Self-Healing Materials. Li et al. presented an SMP-based smart sealant for compression-sealed joints in concrete pavement systems [32]. They also developed an SMP-based syntactic foam that is cored with sandwich structures for the purpose of repeatedly self-healing the impact image [30]. Additionally, they investigated the effects of various design parameters on the closing efficiencies of both pure SMPs and SMP-based syntactic foam [31]. This SMP-based self-healing syntactic foam was successfully tested as a sealant for expansion joint bridges and concrete pavement systems [29, 31, 50, 52, 53]. It was noted that SMP-based foams possessing self-healing properties can also be used in the civil and architectural fields [54]. Therefore, using SMPs as sealants (such as SMP-based, asphalt-based liquid, and two-way shape-changing polymer sealants) has become an important application direction in civil engineering. In addition to sealant applications, the self-healing abilities of SMPs have been also used to form SMP-based composite structures, another important application in civil engineering [55].

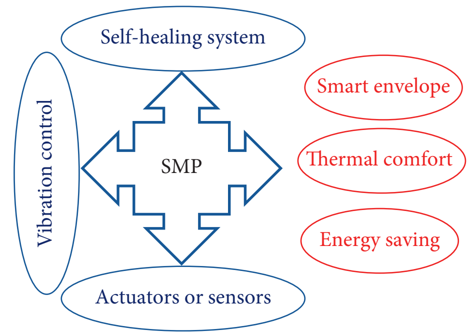

Figure 6: Applications of SMPs in civil and architectural engineering.

3.2. Vibration Control Applications. SMP-based structural components (beams, rods, plates, composites, etc.) allow for the tuning of a range of frequency bandwidths and damping properties for vibration control applications [54–56]. Brown et al. described the fabrication process and dynamic vibration testing of an electrically activated SMP [57]. They demonstrated how SMP beams could achieve variable stiffnesses and damping with a reasonable thermal gradient triggered by electricity. The results showed an approximately 7% shift in the natural frequency and 100% change in the damping ratio of a rectangular SMP beam, which could enhance vibrational performance and expand the operational envelope of structures in the built environment. Another example related to applications of structural vibration control is the tunable hybrid SMP vibration absorbers proposed by Lee et al. [33]. The mechanical and damping properties of SMPs show that SMPs can be used as damping materials, opening the door to vibration control applications in earthquake engineering [58].

3.3. Sensors and Actuators. SMPs have been proposed as a candidate for use in sensors and actuators [57–60]. In particular, SMPs with reversible temperature-sensing capabilities have the potential for structural health-sensing technology applications [61]. DiOrio et al. developed such SMPs, which not only can serve in temperature-sensing applications but also provide a viable route for precisely controlling the shape recovery profile [62]. The experiments conducted by Santo showed promising results for different sized actuator applications in structures where SMAs cannot be used for excesses in the actuation rate or low displacement rates [54]. Yao et al. proposed a feasible method for fabricating SMP composites that could be used as flexible actuators [63]. Catastrophic failure could be prevented by detecting deterioration and potential damage at the early stages, which has long been the main goal of structural health monitoring. SMP composites that could sense the stresses, loads, and other factors imposed upon them would enable the use of embedded sensor and actuator technologies in composite structures, providing structural health monitoring and control during service conditions.

3.4. Requirements and Expectations. From the above survey, it should be noted that the application of SMPs in civil and architectural engineering is still at the early stage, and most existing attempts are in the field of structural engineering. The application of SMPs in architecture requires a wide temperature range, desirable and controllable shape-recovery temperatures, and a large extension rate to fulfill the demands of different environments [35, 59, 61]. The high shape recovery temperatures, relatively low recovery stress, slow recovery rate, and one-way shape memory of most existing SMPs, however, present important and exciting challenges for the application of SMPs in built environments [64]. Table 1 summarizes some SMPs with potential application in built environments. Due to a limited number of contributions to this field, only a few practical examples of potential applications have been given. Also, in Table 1, only a small number of applications have been studied at the experimental stage with in-depth testing and measurements [12, 62]. Conversely, others have so far only briefly been described or proposed in the discussion or conclusion sections of the literature, without actual experiments and measurements [12, 64–71, 75–81].

Possible applications using two-way SMPs have been proposed frequently in recent years. Compared to one-way SMPs, two-way SMPs offer the advantage of being reversible within a particular temperature range. Generally speaking, two-way SMPs have received considerable attention because of their ability to change shapes according to the external stimuli to which they are exposed, and the possibility that they could increase the extension rate via different additions, both of which offer possibilities in built environment applications. We discuss this potential in the following section.

4. Potential of SMPs for Building Energy Saving Purposes

4.1. Kinetic Building Envelopes for Building Energy Efficiency. Highly conditioned buildings via mechanical devices may make such buildings insensitive to the environment and uncouple the building envelope from its role as an environmental moderator. However, this ignores the nature of sustainable buildings and their ability to acclimate (or climatically respond) to the environment, taking full advantage of the positive influences found in nature. In the field of building "acclimation," we found many studies from around the world that addressed building envelopes and their impacts on building energy usage and indoor environment issues. Building envelopes are one of the most important design parameters determining the indoor physical environment, thermal and visual comfort, and even occupant work efficiency; thus, the effect on energy usage is substantial. In particular, the thermophysical and optical properties of building envelopes are factors that should be defined by the materials and geometry of building envelope components. Interest is increasing in net-zero energy buildings, but even current high-performance envelopes can rarely achieve that goal. Most available envelope designs function either as heating or cooling in the dominant climate, but not both. In short, such envelope designs provide less-than-optimal building performance during certain times of year. One way to improve building energy efficiency is to develop kinetic building envelope systems that can alter their thermal and optical properties according to seasonal/daily climatic variations [82]. As more research works related to kinetic buildings have emerged, kinetic building envelope systems have become increasingly likely as a means of defining the optimal climatic responses and heightening indoor comfort. For instance, the developed envelopes with kinetic thermal insulation properties may achieve ~42.6–47.2% cooling and heating energy use savings, relative to the conventional envelopes with static insulation properties in compliance with ASHRAE 90.1-2013 Energy Standard [83].

Importantly, incorporating the shape memory effect into a building envelope component may substantially change its optical and thermal behavior from the point of view of building energy savings. According to the building energy savings mechanism, the behaviors of envelope assemblies including windows, window attachments (i.e., blinds, overhangs, coatings, etc.), wall surfaces, wall insulations, and roof structures are considered an important strategy for responding to external stimuli such as different sun positions, solar radiation levels, wind speeds, temperatures, humidity levels, etc. In order to ensure the significance of such behaviors in a specific envelope component, the stimulus (e.g., temperature, magnetic field, etc.) and application of the SMP must both be considered.

For instance, when it comes to movable window blinds that respond to a variety of solar angles in different seasons (i.e., winter and summer) to potentially utilize or mitigate solar heat gain, a type of thermally responsive SMP can potentially be used in the hinges of the blind structures. The different external air temperatures in winter and summer would then actuate the shape change in the SMP and adjust the angles of the blind slats, as seen in the schematic in Figure 7. Similarly, different SMP layers in a single unit with different T_g values could form various shapes in response to external air temperature changes, which in turn might act as a daylighting control system for potential lighting energy savings, as seen in the schematic in Figure 8. Ideally, these envelope components' changes would be reversible as external stimuli (i.e., temperature, humidity, wind, etc.) are normally periodical. To that end, two-way SMPs show great promise for applications in the fields of dynamic building facades and energy savings. Next, we discuss the mechanisms, properties, and associated possibilities/challenges with two-way SMPs.

4.2. Mechanisms and Properties of Two-Way SMPs

4.2.1. Mechanisms of Two-Way SMPs. According to whether there is a need for an external load for the SMP to operate, two-way shape memory polymers can be classified into two categories: quasi two-way and two-way (see Figure 9) [84].

Not only nematic liquid crystalline elastomers but also single crosslinked (physical or chemical) semicrystalline polymers and their composites can present as two-way SMPs

Table 1: Potential applications of shape memory polymers in built environments.

Potential application	Principle	Reference
Active building facades with self-regulating sun protectors	A broad melting temperature range of temperature-memory polymers based on crosslinked copolymer networks	[12]
Self-shading articulated surfaces	Two-part SMP filaments with different T_g values, forming variable stiffness tiles that respond to different incident solar heat levels	[65]
Smart building envelopes	Integrated conventional one-way shape memory (SM), two-way reversible SM, and one-way reversible SM in semicrystalline SMPs	[66]
Adaptive building envelopes	Significant reversible elongation resulting from crystallization of crosslinked poly(cyclooctene) films under tensile loads and induced cooling or heating	[67]
Functional smart architecture	Under various constant stresses, phase-segregated poly ester urethanes (PEUs) with two-way shape changes between −20°C~60°C	[68]
Convertible roofs	Using a layering technique to combine the SMP and elastic polymer, which forms novel polymer laminates with a two-way shape-memory effect (two-way SME)	[69]
Interactive kinetic walls	Reversible actuation of ultrathin semicrystalline polymer films (e.g., thin polycaprolactone-gelatin bilayer films that can be unfolded at room temperature, folded at a temperature above the polycaprolactone melting point, and unfolded again at room temperature)	[70]
Ecological architecture	Bidirectional shape memory polymers that can become repetitively actuated two-way SMPs under stress-free conditions	[71]
Changeable architecture	The design and fabrication of polymer particles with two-way SMP abilities between 0°C~43°C under stress-free conditions	[72]
Thermally comfortable buildings	Copolymer networks from oligo (ε-caprolactone) an n-butyl acrylate that enable a reversible bidirectional SME at human body temperature	[73]
Decorative architecture	Larger prestretching of two-way SMPs that can achieve longer actuator lengths without a constant external load	[74]
Intelligent buildings	SMPs with various macromolecular architectures including linear, three-, and four-arm star poly (ε-caprolactone) that are functionalized with methacrylate end-groups and two-way SMPs; the amount of recovered strain and the time required are decided by the combination of melting, deformation, and recovery temperatures	[75, 76]
Hybrid solar-thermal facades	Optimization of the load and phase morphology, especially the separation/decoupling of blend phases of SMPs, which increases the crosslink density and crystallinity of polymer networks, further enhancing the SME of the SMPs	[77]
Ecological building systems	Fabrication of two-way SMPs with "switch-spring" composition by interpenetration of the polymer network	[78]
Self-regulating shading systems	Higher gel fractions (above 75%) of semicrystalline elastomeric networks in SMPs achieving a two-way SME at low room temperatures	[79]
Architecture-based energy savings	Carbon black nanoparticles have the ability to lower the response temperature range of polyethylene-based SMPs and maximize the actuation ratio selection via optimal loading	[80]

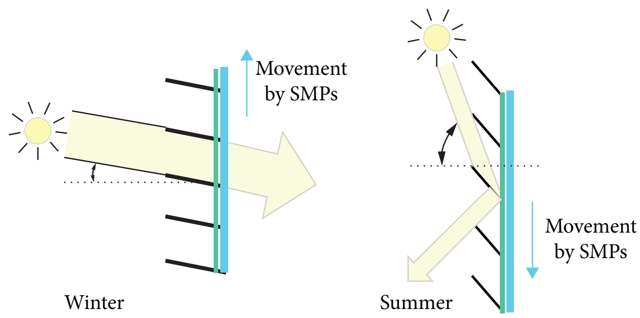

Figure 7: Schematic diagram of thermally responsive SMPs in heat controls of window blinds.

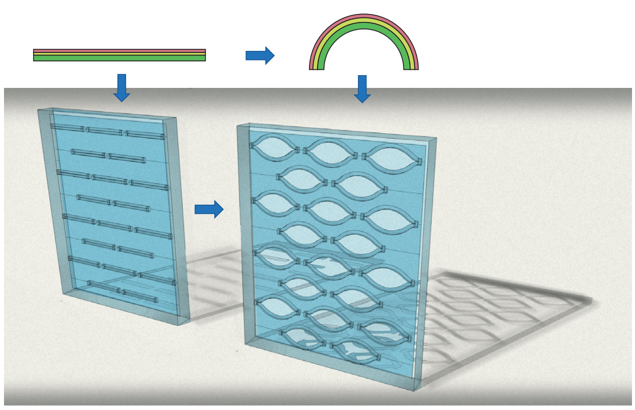

Figure 8: Schematic diagram of composite SMPs in shading controls.

under constant external loads [85]. The mechanism for the nematic liquid crystalline elastomers is that the ordering of mesogenic moieties and elastic properties of liquid crystalline elastomers enable a two-way SME in the liquid crystal elastomer. Heating a nematic liquid crystalline elastomer through the nematic-isotropic transition results in the constituent prolate network chain characteristic of the nematic state, contracting it to the spherical configuration of the isotropic phase. A large macroscopic contraction of more than 100% occurs simultaneously. This contraction is reversed upon cooling back to the nematic phase [18].

However, it is necessary for a polydomain nematic liquid crystalline elastomer leading to a two-way SME to apply a finite (~50 kPa) stress [85]. Thermal-responsive semicrystalline polymers must be subjected to a constant stress to yield a two-way SME. Similarly, the mechanism behind this for thermally responsive SMPs is the transition between the amorphous and crystalline phases. While cooling elongates the crystallization of a semicrystalline polymer under a tensile load, the crosslinked entropy elastic modulus of the amorphous phase decreases, as does the capability of the bearing force of the semicrystalline (amorphous + crystalline phase) polymer, which results in elongation. The shape recovery will be achieved by heating to melt the network subsequently [18, 74, 82].

Nonetheless, the external load greatly limits wider application of two-way SMPs. Some polymer laminates, two-way SMPs, and their composites can achieve driving force due to an internal force or the anisotropic network. Therefore, they do not need an external force while in operation [84]. A two-way SMP can produce a two-way SME without an external load when it combines chemical and physical crosslinked networks during the synthesizing process, and this is called a dual network. The chemical crosslinks secure the memory of the original shape while heating, and the physical crosslinks restore the temporary shape during cooling [66]. Polymer laminates completely combine ordinary polymers, elastomers, or SMP composites into a thin film, layer by layer. Different properties of composite materials such as the elastic modulus may cause different recovery stresses, resulting in a driving force bending the shape of recovery [69]. Similarly, two-way shape memory polymer composites (SMPCs) synthesize SMPs together so that they form a long molecular chain polymer. The mechanism is the ordering of the crystalline segment and elastomeric network, which enables the two-way SME of SMPCs. The preprogramed crystalline segment melts into the amorphous phase through a glass-rubbery transition. The movement of the crystalline segment is balanced with the crosslinked network to present a simultaneous shrinkage. During the crystallization, the balance is broken by the stored energy in the elastomeric network, providing the driving force for shape recovery [78].

4.2.2. Properties of Two-Way SMPs. Many properties (including thermal, mechanical, and shape memory) of two-way SMPs have been studied [70, 83–85]. Properties are important factors impacting the performance of two-way SMPs in different fields. This review focused on thermally responsive SMPs in built environment applications. Therefore, the temperature range was our first concern, because that built environment temperature decides the feasibility of a two-way SMP. The extension rate was another important consideration, due to the maximizing flexibility of applications for two-way SMPs.

Temperature range is an important thermal property of two-way SMPs. Different materials involved with SMPs present different temperature ranges. Figure 10 lists thermally responsive two-way SMPs, temperature ranges for their reversible shapes, and their transition temperatures. The SMPs listed in Figure 10 include six-arm polyethylene glycol-polycaprolactone (6A PEG-PCL), polyethylene-co-vinyl acetate (cEVA), semicrystalline poly ε-caprolactone (cPCL), crosslinked polyethylene (cPE), 1,6-hexamethylene diisocyanate (HMDI) + PCL + 1,4-butanediol (BD) (HPL), oligo ε-caprolactone (OCL), polycaprolactone (PCL)-gelatin, PCL-poly tetra-methylene ether glycol (PCL-PTMEG), poly cyclooctene-dicumyl peroxide (PCO-DCP), polydopamine-poly ε-caprolactone (PDA-PCL), poly ester urethane (PEU), poly octylene adipate (POA), poly pentadecalactone-poly ε-caprolactone (PPD-PCL), and preelongated shape memory polyurethane with unelongated elastic polyurethane (SMPU-PU). All SMPs shown in Figure 10 had a temperature range minimum to maximum from −20 to 100°C. Among the thermal properties of each material, transition points T_g or T_m were the critical features

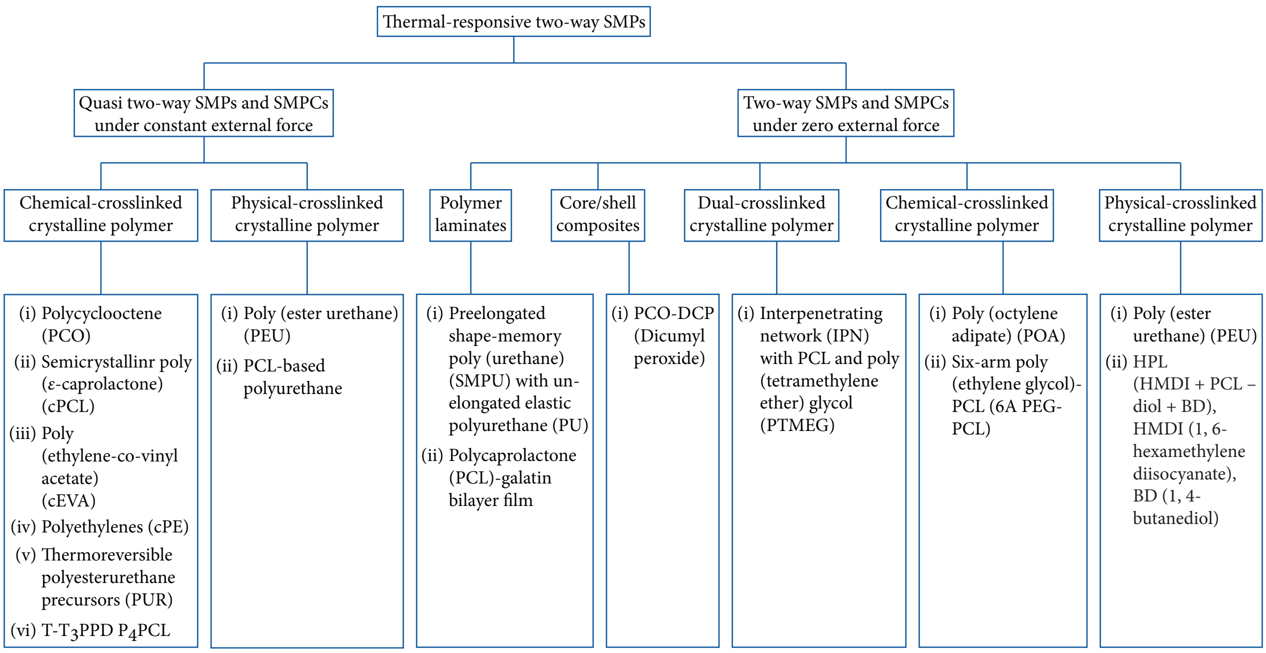

FIGURE 9: Thermally responsive two-way SMPs.

influencing this temperature range. Figure 10 clearly indicates that the temperature range of the poly ester urethane (PEU) was widest among all of the considered materials. PEUs can detect a two-way SME between +60 and −20°C while under a tensile load [65]. Meanwhile, a trained PEU specimen can display a two-way SME cycle between +60 and −10°C under zero external load [86]. Therefore, the temperature range of a PEU covers the built environment temperature. Zhou et al. presented a semicrystalline elastomers—poly octylene adipate (POA) with a temperature between 5 and 38°C, which was close to the built environment temperature [66]. The temperature range of a POA is narrower than that of a PEU, so that a POA may not be usable in some complicated environments. Thus, PEUs are regarded as the best candidate polymer type for the application of two-way SMPs in built environments, because they have a wide temperature range and are stress-free.

In addition to the temperature features, the extension rates of two-way SMPs and SMPCs are another important feature that indicates the shape-changing possibilities. Bothe found the extension rate of a PEU to be $\sigma = 1.5$ MPa (external load) up to 37% [68]. The researcher also explained that the maximum extension rate of a trained PEU with zero external load could reach 36% [87]. Ma et al. found that pure crosslinked polyethylene (cPE) has a 21.3% extension rate [80]. SMPCs and polymer laminates usually have smaller extension rates. For example, poly ε-caprolactone- (PCL-) based materials can achieve elongation (extension) up to 25% [75]. Stoganov et al. described a PCL-gelatin polymer laminate with a ~10% extension rate [70]. It was determined that the extension rates of two-way SMPs and SMPCs can range from ~10% to 37% [65, 75, 80, 86]. PEUs under external loads have the largest extension rates of all, which makes it possible that PEUs as two-way SMPs could be flexibly applied in built environments.

4.3. Challenges to Using Two-Way SMPs in Dynamic Building Envelopes. Two-way SMPs have excellent properties such as lightweight and reversible shape changing abilities, but there are also challenges to their application in built environments, among which the following three aspects are worth mentioning for future research [66, 77].

4.3.1. Tradeoff between Extension Rate and Transparency. A 100% extension rate with a high level of transparency is desirable so that two-way SMPs can be applied to dynamic building envelopes. However, it is extremely difficult to achieve this goal. Bothe found that an external load affected the elongation of a PEU; the largest was 37% under a certain tensile load, but the researcher did not develop a numerical model to simulate the relationship between the external load and extension rate [68]. Ma et al. concluded that the addition of carbon black (CB) would greatly decrease elongation. Adding 20% vol. CB to pure cPE, the extension rate decreased from 21.3% to 15.7% [80]. Kolesov et al. studied crosslinked polyethylene (PE)/PCL, and concluded that an increased crosslink density and crystallinity in the polymer network could enhance a two-way SME, as well as the selection of optimal loads [77]. Nevertheless, several studies have examined the relationship between the extension rate and transparency of two-way SMPs, and the impact factors (such as external load, additions, crosslink density, and crystallinity) most affecting them. Better transparency provides improved natural lighting. However, additions to two-way SMPs to increase the extension rate may cause a lower level of transparency. Balancing addition and transparency means a tradeoff. Thus, understanding the relationship between external load and extension rate in two-way SMPs, as well as the key impact factors, are challenges to the broader application of two-way SMPs in built environments.

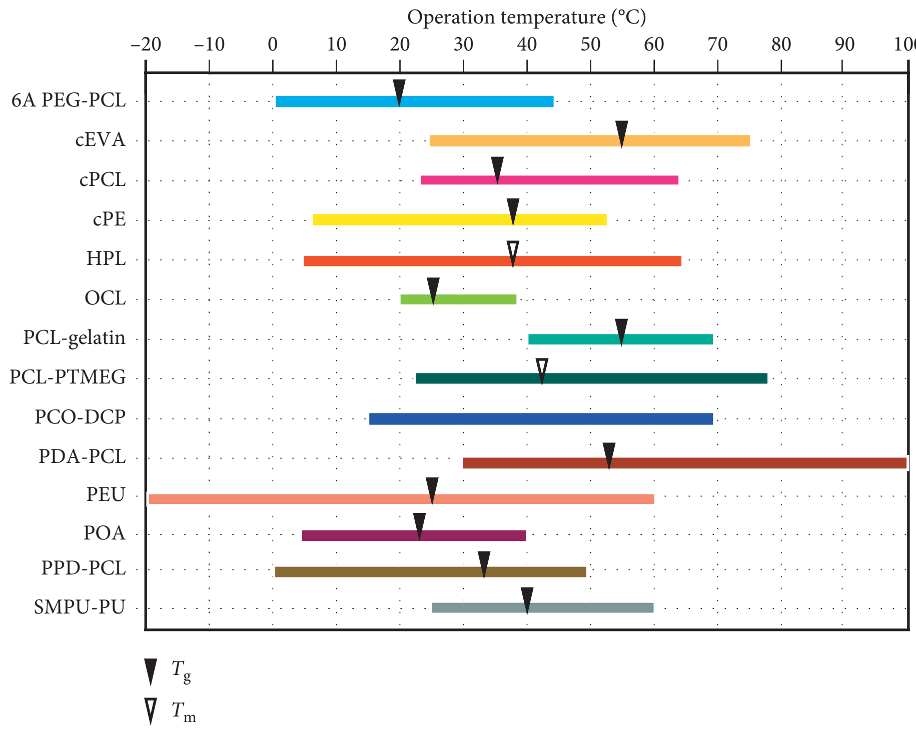

Figure 10: Temperature ranges of thermally responsive two-way SMPs.

4.3.2. Methods and Designs for Ideal Temperature Ranges. It is appropriate in the application of two-way SMPs and SMPCs in built environments for the accurate temperature to range from −15 to 40°C. Two-way SMPs will not respond below the lower temperature range, T_L, and they become irreversible at a temperature point just a little bit higher than the upper temperature range, T_H [66]. Some researchers have studied different methods of changing the temperature ranges of two-way SMPs. Tunable actuation temperatures with two-way SMPs via a photo-crosslinking (UV) method have served to increase the T_H by about 25°C because of the addition of photo-crosslinks [88, 89]. Adding CB to two-way SMPs is also an available approach to affect the operation temperature [80]. Another approach is using polymer laminates such as shape memory polyurethane (SMPU)/PU and PCL-gelatin to change the temperature range [66, 75]. However, none of this research has provided a numerical model to illustrate the impact factors (such as UV, CB, and the composite layer) on the temperature range of reversible cycles. Even though it was determined that the temperature range of a PEU covers the built environment temperature, it is still a challenge to find a PEU with a precise temperature range from −15 to 40°C.

4.3.3. Fabrication Methods for Microstructure Design. A two-way SMP with a reasonable microstructure, such as composing different SMPs into one device, could possibly change their original properties, thus applying in dynamic building envelopes. However, fabricating appropriate two-way SMPs can be difficult. A novel polymer fabrication process using 3D printing has recently emerged [77, 87, 90–92]. 3D printing is capable of producing advantageous complex structures. With the help of SMPs, 3D printed materials are able to respond to and change shape with a stimulus and this is called 4D printing (self-enveloping/self-folding) [77, 87, 90, 91]. This 4D printing technique was first presented in a water solution but was nonreversible [93]. Ge et al. introduced their design for 4D printing laminates producing a one-way SME in air [94]. Naficy et al. investigated polyether-based polyurethane with hydrogel structure using 3D printing, resulting in a two-way SME in water [82]. Therefore, this novel 3D/4D technique makes possible the fabrication of desirable two-way SMPs with multiple layers or specific microstructures. Nonetheless, it is still a challenge to determine the fabrication process for two-way SMPs in built environments because 3D printed two-way SMPs have thus far only been used in water environments.

5. Conclusions

Smart materials have been applied in building structures and envelopes for various purposes that require specific combinations of optical, thermal, and mechanical properties. In the current work, the general principles of SMPs were described, and previous research with selected application examples in built environments were categorized and reviewed. Special emphasis was given to the potential use of two-way SMPs as adjustable structures for building energy efficiency. Two-way SMPs used in buildings must meet weather and/or room temperature ranges. In addition, properties such as extension rate, transparency, design characteristics, and compatibility with envelope assemblies also need to be considered. From both experiments and simulations, it is clear that incorporating SMPs into building structures offers the potential to improve building envelope structures and environmental performance. However further investigations are needed into the development of particular two-way SMPs by material scientists and engineers working collaboratively with architectural and structural researchers. Once that work is completed, building designers and engineers can focus on methods for incorporating SMPs, embedding them into existing building structures and envelope assemblies, long-term stability, and any other problems affecting the safety, reliability, and practicability of the thermal energy storage used in buildings.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

Jing Li, Qiuhua Duan, and Enhe Zhang have equally contributed to this paper.

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