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EDITORIAL

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Shape Memory Polymers: Ever Evolving Shape Morphing Characteristics

Shape memory effect (SME) of polymers refers to their ability to fix temporary shapes and revert to their permanent shapes in an on demand fashion. Whereas the permanent shape is typically determined by the molding processes, the temporary shape(s) can be arbitrarily defined by an external force applied during the programming step (or shape fixing step). This attribute differentiates shape memory polymers (SMP) from many other classes of stimuli-responsive shape-changing polymers, in terms of both the material behaviors and potential applications.

Recognition of polymer SME can be traced back to 1940s. The best known commercial SMP product (heat-shrink tubing) by Raychem Corporation emerged in the late 1950s, which has since been widely used in various industrial sectors. Other similar commercial products such as heat-shrink labels and shrink-dink toys are also available in today's market. Despite the early commercial success, fundamental research of SMP was significantly behind in the last century. This was mostly reflected in two aspects. First, the molecular requirements of the basic polymer SME were incorrectly stated in early literature. The most popular statement was that SMP should possess both a reversible phase and a frozen phase that are respectively responsible for fixing the temporary shape and defining the permanent shape. This implies the requirement for a two-phase polymer system. In reality, any polymer with a reversible phase transition coupled with either physical or chemical crosslinking would suffice. The former allows reversible activation of the molecular segmental mobility for temporary shape fixing and the latter ensures memorization of the permanent shape. Thus, the combination of switchable segments and a network structure represent more accurate description of the molecular requirement for SMP, which was proposed in 2011.[1] This is non-trivial as it implies any network polymers with a reversible thermal transition are expected to have shape memory characteristics. In addition, thermoplastic polymers with a physically crosslinked network or being modified by chemical crosslinking would also readily meet the criteria. The new description correctly points out the fact that SME is not unique for a small set of multi-phase polymers, but can be expected for most (if not all) polymers. Indeed, viewing from a different angle, SME originates from the viscoelastic effect intrinsic to polymers. The improved understanding of the SMP is key to its development, not only in expansion of material classes but also in discovery of versatile shape memory behaviors. The second and rather notable deficiency of the SMP development in the last century lies in the lack of advanced functions beyond direct heating triggered one-way shape-shifting between a temporary shape and the permanent shape. This is now classified as one-way dual-shape effect to distinguish with many other new SMEs discovered in the 21st century. Spurred by the realization of SMP's vast technological potential mainly in medical and aerospace applications, significant progresses have been made in the last fifteen years or so. Most of the recent advances (*e.g.*, multi-shape effect, thermadapt SMP, and 4D printing) have been extensively reviewed in recent literature. In this editorial, the author intends to discuss selectively a few important aspects that have not received sufficient attention in recent reviews.

In many materials research areas, a few performance parameters can be used to judge the superiority of materials such as efficiencies for solar cells or ZT values for thermoelectric materials. This is not the case for SMP. An SMP can be quantitatively evaluated by its shape fixity ratio, shape recovery ratio, recovery speed, recovery stress, and maximum strain. Both the shape fixity and shape recovery ratios approach 100% for many SMPs and are therefore not good performance differentiators. The latter three reflect the complexed and diverse requirements of SMP. For the maximum strain, most typical SMP applications do not require a very high strain. Shape memory alloys, for instance, typically have a maximum strain less than 10%. This low strain capability has not prohibited their commercial use since many large geometric changes such as bending and twisting are associated with small strains. There is no question that the potential for SMP to be designed to have very large strains even beyond 2000% is an advantage over shape memory alloys, but this may not be the most relevant performance parameter in currently known application scenario. Similarly, one might intuitively think that faster recovery and higher recovery stress are beneficial. Indeed, these two performances are relevant for many applications and have been the subjects of many scientific papers. However, the opposite performances (*i.e.*, slow recovery and low recovery stress) may become useful for certain future applications, especially medical devices. A hypothetic case is a deployable neuron probe based on an SMP substrate. Unless delivered by a syringe, its insertion into brain tissues requires the probe to be sufficiently rigid. After insertion, however, the deployment needs to be extremely slow and should generate a sufficiently small stress so as not to damage the surrounding tissues. Although this example represents an extreme case, there are many other cases for which faster recovery and higher recovery stress are not needed.

An area of active SMP research over the last two decades has been the development of non-direct heating methods as alternative stimulation for triggering shape recovery. Various approaches have been proven effective, including resistive heating, photo-thermal conversion, and induction heating *via* AC magnetic field. There are also efforts to develop SMP that can be triggered by multiple methods, the so-called multi-stimuli responsive SMP. Al-

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though these capabilities may be useful under certain circumstances, having to access these stimuli adds complications. Induction heating for instance requires the SMP to be in close proximity to a bulky AC magnetic generator, which severely limits its potential. As such, an opposite thought deserves more attention, that is, how to realize controllable SMP recovery with minimum or even no external intervention. This would greatly ease the burden for device applications. Water-triggered SMP demonstrated by Prof. Weimin Huang's group is a prime example in this regard.[2] Instead of heating, it relies on water as the plasticizer to reduce the glass transition temperature to trigger recovery. Since water is naturally present in human bodies, the device can in principle operate without having to supply any form of heating. The athermal SMP recently reported by Prof. Yanlei Yu's group represents an interesting example in a different way.[3] They show that light triggered isomerization of azobenzene moieties results in reversible reduction of the glass transition temperature. This enables athermal SME without requiring any temperature change in both the shape fixing and recovery steps. Along the same line, the recently emerged temporal SMP is particularly noteworthy. By controlling the duration of the external stress imposed on supramolecular SMP in the shape fixing step (*i.e.*, the programming time), the stored entropic energy can be varied *via* supramolecular bond exchange in the network. The material is either a hydrogel (Prof. Sergei Sheiko's group)[4] or an elastomer (our group)[5] that naturally recovers upon stress removal (no heating), with the recovery speed determined by the programming time. Thus, this approach does not rely on any thermal transition and employs no external stimulation for recovery. It simply utilizes the most natural stimulation (time) to control the shape-shifting. Despite their elegance, it should be noted that the above examples all have their own sets of limitations, they nevertheless represent an intriguing future direction.

Although traditional SMPs display only one-way SME, two-way (or reversible) SMP has recently gained increasing attention. The underlying behavior here is that, for a crystalline network under a constant external stress, it exhibits reversible shape-shifting behavior *via* crystallization-induced elongation and melting-induced contraction as revealed by Prof. Patrick Mather's group.[6] The external stress can be replaced by an internal stress locked into the network by either a physical phase transition (Prof. Andreas Lendlein)[7] or chemical crosslinking (our group),[8] thus realizing (external) stress-free two-way SME. This is very similar to mesogen alignment behind the reversible shape-shifting behavior of liquid crystalline elastomers. Comparatively, crystallization based two-way SMP is advantageous in the flexibility of tuning the transition temperature. However, it falls short in its much more pronounced thermal hysteresis, meaning that the reversible shape-shifting has to occur at a wider temperature window relative to liquid crystalline elastomers. The stress-free reversible shape-shifting is often viewed as being more advanced than that under a constant stress. From a mechanics viewpoint, however, this could be somewhat a misconception. The stress-free shape-shifting cannot generate large forces, but the external stress induced shape-shifting can. Of course, which of the two behaviors is more relevant would depend solely on the target application.

To summarize, it is important to note that potential SMP applications especially those off the radar screen may require very different or even opposite shape-morphing characteristics. The beauty is that one cannot foresee what might emerge in the future. One can argue what is desired, but the author holds the opinion that there is not much undesired unless it is uncontrollable. In many ways, viewing things from different angles is the key. The programmable shape-morphing behaviors of SMP, regardless of the versatility and uniqueness, all originate from polymer viscoelasticity. It is the innovative application of this simple yet general principle that would be behind most if not all things ahead.

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