

Copyright

By

Eugene Patrick Sunday

2012

The Report committee for Eugene Patrick Sunday

Certifies that this is the approved version of the following report:

Shape memory polymers:

The Wave of the Future or a Passing Fad?

APPROVED BY

SUPERVISING COMMITTEE:

Supervisor: _____

Isaac Sanchez

Thomas F. Edgar

Shape Memory Polymers:

The Wave of the Future or a Passing Fad?

by

Eugene Patrick Sunday, B.S. Chem Eng.; J.D.

Report

Presented to the Faculty of the Graduate School

of the University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science in Engineering

The University of Texas at Austin

December 2012

Dedication

This paper is dedicated to my wife, Heather, and our children for without their love, encouragement and support I would not have completed this effort.

I would like to further acknowledge the support and guidance offered by the faculty of the Chemical Engineering Department at the University of Texas at Austin. Without their support, time, and encouragement would not be able to complete this process.

Abstract

Shape Memory Polymers:

The Wave of the Future or a Passing Fad?

by

Eugene Patrick Sunday, M.S.E.

The University of Texas at Austin, 2012

SUPERVISOR: Isaac Sanchez

New materials always have the possibility of revolutionizing manufacturing processes and the way we live. Bronze, steel alloys, vulcanized rubber, ceramics, and fiber optic cables are just a few of the materials man has discovered which improved his quality of life. One of the more recent additions to the field of material science are materials that exhibit what is known as the shape memory effect. Both metals and synthetic polymers can acquire this property through processing and chemistry. However while shape memory polymers hold a lot of promise, it will require more research and development to make them affordable and useful in large scale applications.

Table of Contents

I. Introduction.....	1
A. The Discovery of the Shape Memory Effect in Metals.....	1
B. How Shape Memory Alloys Work.....	2
1. Normal Transformation from Martensite to Austenite.....	2
2. How the Memory Effect is created in Shape Memory Alloys.....	5
C. Shape Memory Alloys Types.....	8
1. Nitinol.....	8
2. Other Shape Memory Alloys.....	8
II. Shape Memory Effect in Polymers.....	12
A. Shape Memory Polymer History.....	12
B. Shape Memory Polymer Basics.....	15
1. The Basic Shape Memory Polymer Cycle.....	16
2. So What is a Shape Memory Polymer?.....	21
C. Shape Memory Polymer Composites.....	23
III. Types of Shape Memory Polymers and Activation Methods.....	24
A. Polyurethanes.....	24
1. Chemistry.....	25
2. Processing.....	25
3. Structure.....	26

B. Epoxy.....	27
1. Chemistry.....	27
2. Processing.....	29
3. Structure.....	30
C. Maleimides.....	31
1. Chemistry.....	32
2. Processing.....	34
3. Structure.....	35
D. Acrylates and Styrene Based.....	36
1. Chemistry.....	37
2. Processing.....	38
E. Activation Mechanisms.....	39
IV. Coming Future Developments.....	42
A. Three Way Shape Memory Effect.....	42
B. Four Way Shape Memory Effect.....	48
V. Conclusion.....	53
References.....	55

Shape memory polymers: The Wave of The Future or a Passing Fad?

I. Introduction

Shape memory polymers were first discovered in Japan in the early 1980's and exhibited properties that, at the time, were unique to polymers, but not unknown in the field of material science.¹

Memory effect, or the ability to recover an original, casted shape under a stimulus, was known to exist in metals, commonly referred to as shape memory metals (SMAs), but not polymers.² Over seventy five years of research has led to new and better understanding of how SMAs work and achieve the shape memory effect. The production costs of SMAs remain high, placing a large-scale, practical application of SMAs still out of the reach of the common consumer.

A. The Discovery of the Shape Memory Effect in Metals

The first reported steps towards the discovery of the shape-memory effect were taken in the 1930s. In 1932, Ölander discovered the pseudoelastic behavior of the Au-Cd alloy.³ In 1938, Greninger and Mooradian (1938) observed the formation and disappearance of a martensitic phase by decreasing and increasing the temperature of a Cu-Zn alloy.⁴ The

basic phenomenon of the memory effect in metals is governed by the thermoelastic behavior of the martensite phase and was widely reported a decade later by Kurdjumov and Khandros (1949) and also by Chang and Read (1951).⁵ This property was highly surprising and led to more research into how this effect is achieved.

B. How Shape Memory Alloys Work

Shape memory alloys (SMAs) rely on the transformation of the crystal lattice of the metal from an austenite to martensite phase to lock in deformation and a reverse of the process to recover a memory shape. The austenite phase is typically defined as the phase at which a solid recrystallizes and has a face-centered cubic crystal structure.⁶ The martensite phase is characterized by a body-centered tetragonal crystal structure.⁷ It is the differences in the crystal lattice structure of these two phases which can, but does not always, give rise to the shape memory effect.

1. Normal Transformation from Martensite to Austenite

The transition between the austenite and martensite phase structures requires very little thermal activation energy because it is a diffusionless transformation. The transformation is due to a small and a macroscopically imperceptible, but rapid rearrangement of atomic positions; and has been known to occur even at cryogenic temperatures.⁸ Martensite has a lower density than austenite, so that the martensitic transformation

results in a relative change of volume.⁹ Of considerably greater importance than the volume change is the shear strain which determines the shape of the plates of martensite.¹⁰

Each martensitic crystal formed can exist in one of two forms, twinned or de-twinned.¹¹ The reversible phase transformation from austenite to martensite and back is the basis of the unique behavior of SMAs; however, without external conditions acting upon the SMA, simple heating will not trigger the shape memory effect. Thus, upon cooling in the absence of an applied load, the phase transition from austenite to martensite will result in a twinned martensite phase in the SMA.¹² Once the SMA is reheated the twinned martensite will revert to an austenite phase with no associated shape change.¹³

Figure 1 below shows the transition from austenite to martensite phases versus temperature. In Fig. 1, M_s is the temperature at which the transition to the martensite from austenite begins and M_f is the temperature at which the transition to martensite completes upon cooling. Accordingly, during heating A_s and A_f are the temperatures at which the transformation from martensite to austenite starts and finishes. The symbol ξ represents the fraction of the material in the martensite phase.

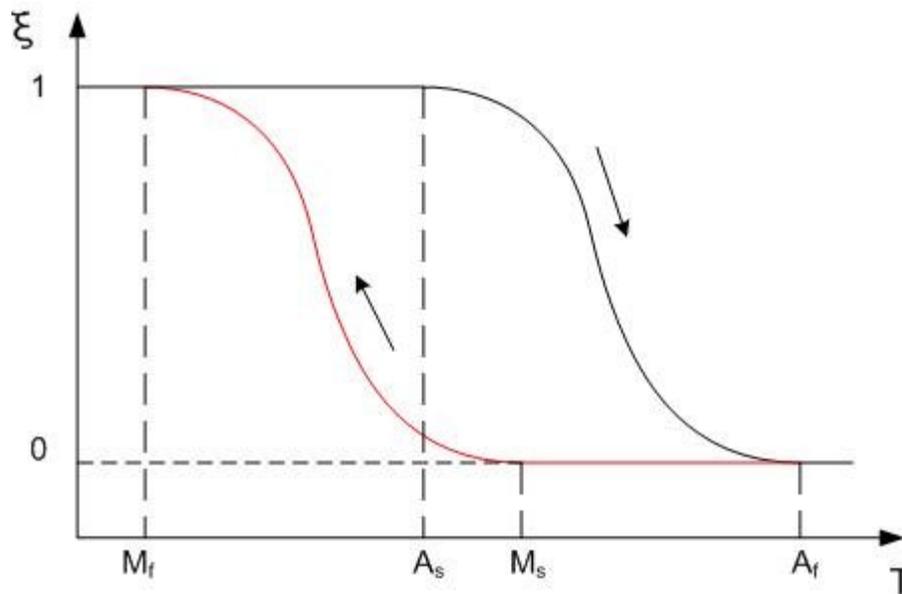


Figure 1. Temperature Vs. Fraction of Martensite Phase Crystal Lattices

Transition temperatures for SMAs are the temperatures at which the transformation from martensite to austenite starts and finishes. This martensitic reaction begins during cooling when the austenite reaches the martensite start temperature (M_s) and the parent austenite becomes mechanically unstable. At a constant temperature below M_s , a fraction of the parent austenite will transform rapidly, then no further transformation will occur. When the temperature is decreased, more of the austenite transforms to martensite. Finally, when the martensite finish temperature (M_f) is reached, the transformation is complete. Martensite can also be formed by

application of stress. Thus, Martensite can be thermally induced or stress induced (also known as pseudo-elasticity).¹⁴

2. How the Memory Effect is created in Shape Memory Alloys

The unique shape memory effect is made possible through a solid state phase change, or a molecular rearrangement, which occurs in a shape memory alloy. The first idea that normally comes to mind when the term phase change is mentioned is a change from a solid to liquid or liquid to gas. A solid state phase change is similar in that a molecular rearrangement is occurring, but the molecules remain closely packed so that the substance remains a solid.¹⁵ In most shape memory alloys, a temperature change of only about 10°C is necessary to initiate this phase change. In the case of SMAs this phase change occurs between the martensite and austenite phases. A molecular view of this change is shown in Figure 2.



Figure 2. Microscopic View Austenite and Martensite Phases¹⁶

Martensite, is the relatively soft and easily deformed phase of shape memory alloys, which exists at lower temperatures. The molecular structure

in this phase is twinned, the configuration of which is shown in the center of Figure 2. Upon deformation, this phase takes on the form shown on the right of in Figure 2. Austenite, the stronger phase of shape memory alloys, occurs at higher temperatures or under load. The shape of the Austenite structure is cubic, the structure shown on the left side of Figure 2. The un-deformed Martensite phase is the same size and shape as the cubic Austenite phase on a macroscopic scale, so that no change in size or shape is visible in shape memory alloys until the Martensite is deformed.¹⁷

SMA's become a shape memory material when a load is applied to the material in the twinned martensitic state. With a load, the twinned martensite are reoriented to a detwinned phase which results in a microscopic shape change where the deformed, or detwinned state, is retained when the load is released. A subsequent heating of the SMA pushes the martensitic sites to an austenitic phase and a recovery of the original shape. Cooling of the SMA from the austenite phase to the martensite phase, with no load applied will allow the SMA to retain its memory shape.¹⁸

Figure 3 is a representation of the shape memory effect in SMA's.

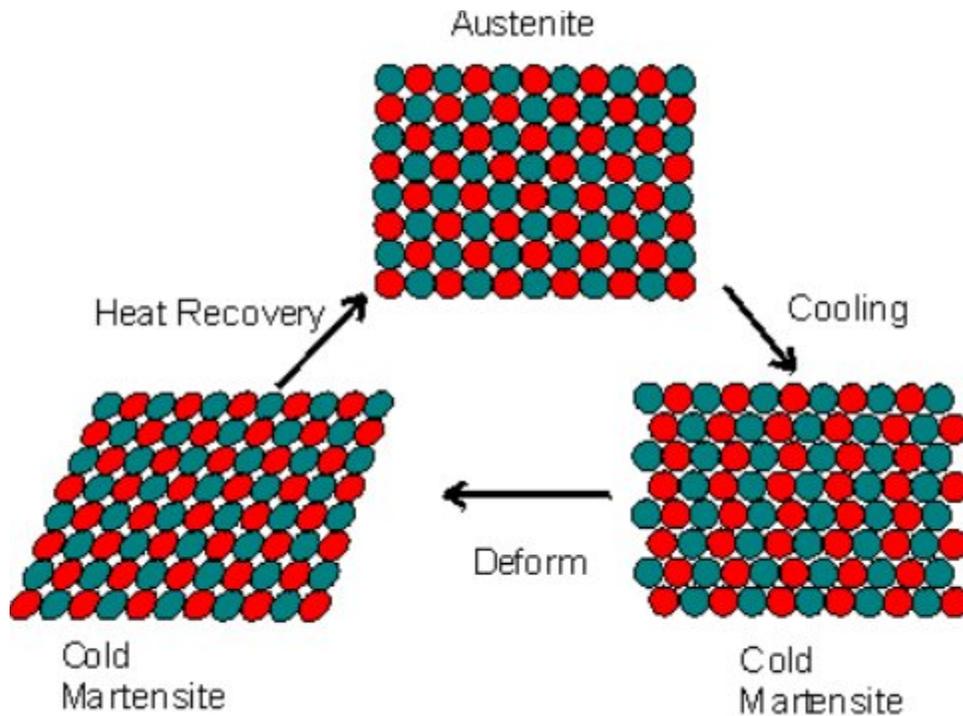


Figure 3. A representation of the Shape Memory Effect in SMAs.

The transition from the martensite phase to the austenite phase is only dependent on temperature and stress, not time, as most phase changes are, as there is no diffusion involved. Similarly, the austenite structure receives its name from steel alloys of a similar structure. It is the reversible diffusionless transition between these two phases that results in special properties. While martensite can be formed from austenite by rapidly cooling carbon-steel, this process is not reversible, so steel does not have shape-memory property.¹⁹

C. Shape Memory Alloy Types

Shape memory alloys exist in several types. Nitinol is the most common type in research, but is the most expensive. Other shape memory alloys can be made of cheaper metal, but they have not gained main stream acceptance because of the high cost of processing.

1. Nitinol

The first shape memory metals were first developed in the early 1960's by the United States Naval Ordnance Laboratory. These nickel-titanium metals were commercialized under the trade name Nitinol (an acronym for Nickel Titanium Naval Ordnance Laboratories). As with many major discoveries, the remarkable properties of Nitinol were discovered by accident. A sample that was bent out of shape many times was presented at a laboratory management meeting when one of the associate technical directors, Dr. David S. Muzzey, decided to see what would happen if the sample was subjected to heat and he held his pipe lighter underneath it. To everyone's amazement the sample stretched back to its original shape. This discovery allowed the creation of shape memory alloys such as Nitinol and copper-aluminum-nickel alloys.²⁰

2. Other Shape Memory Alloys

The other two main types of shape-memory alloys are based on a copper-aluminum-nickel alloy and alloys of zinc, copper, gold and iron.²¹

Cu-Al-Ni SMA's are popular due to their wide range of useful transformation temperatures and small hysteresis. They are also the only SMA's that can be used at temperatures over 100°C. Compared to Ni-Ti SMA's, the CuAlNi alloys are much cheaper to make as they use cheaper raw materials and do not require sophisticated processing as do the NiTi alloys.²²

CuAlNi SMA's usually contain between 11% and 14.5% aluminum and between three and five percent nickel, with the balance being copper. The aluminum content strongly influences the alloys' transformation temperature. Reducing the aluminum content below 12% can also improve the alloys' mechanical properties. Adding manganese (approximately two percent) can reduce the transformation temperature, while the addition of small quantities (approximately one percent) of boron, cerium, cobalt, iron, titanium, vanadium and zirconium are also commonly added to control grain size.²³

Copper-Zinc-Aluminum was the first copper based SMA to be commercially exploited and the alloys typically contain between 15% and 30 wt% Zn and between three and seven weight percent Al. The useful transformation temperature for this system ranges from -100°C to +100°C; the actual transformation temperature is a function of both the alloy

composition and the thermomechanical treatments applied during its manufacture.²⁴

The major advantage of the CuZnAl alloys is that they are made from relatively inexpensive metals by conventional metallurgical processes which makes them the cheapest of the commercial SMAs. However, their memory properties are modest with a maximum recoverable strain of about five percent. The ternary alloys also have a very large grain size which makes them brittle, but the addition of less than one percent of a grain refiner such as titanium or zirconium limits the grain size and solves the brittleness problem. The major disadvantages of this alloy system are that the martensitic phase is stabilized by long term aging even at room temperature causing an increase of the transformation temperature, and the alloy structure decomposes when exposed to temperatures above 100°C. These disadvantages have more than outweighed the cost advantage of the CuZnAl alloys and this alloy system is rarely used today.²⁵

Copper-aluminum-nickel (CuAlNi) alloys have undergone extensive development and are now preferred to the CuZnAl alloys. The alloys typically contain between 11% and 14.5% Al and 3% and 5% Ni and have transformation temperatures in the range 80°C to 200°C dependent on their composition because the transformation temperature is particularly sensitive to the aluminum content.²⁶

This alloy is again made from relatively inexpensive elements, but its processing is more difficult since it can only be hot worked and the final heat treatment has to be tightly controlled to produce an alloy with the desired transformation temperature. These processing difficulties have made this alloy system more expensive than CuZnAl, but it is still less expensive than NiTi. The ternary alloy Cu₁₃Al₄Ni is the one that is often used commercially.²⁷

Some improvement of the mechanical properties can be obtained by reducing the aluminum content below 12%, adding 2% manganese to reduce the transformation temperature and 1% titanium as a grain refiner but these additions can affect the stability of the alloy structure.

The major advantages of the CuAlNi system are its wide range of useful transformation temperatures, its stability at elevated temperature making it the only system that can be used for applications above 100°C, its small hysteresis, and its relatively low cost.²⁸

This shape memory effect has been well documented and commercially exploited. Unfortunately, the lack of usable shape change, typically less than eight percent in SMAs, and the extreme cost of the materials have made SMAs a very impractical solution for large scale processes and devices.²⁹ Thus, the need for a cheap and mechanically practical material existed.

II. Shape Memory Effect in Polymers

Synthetic polymers can typically be made for much less than processed metals and can offer similar properties in some cases. The discovery of shape memory polymers in 1984 created a new class of smart materials that offered mechanical action triggered by an external stimulus. Like SMAs, shape memory polymers are able to “remember” one or more shapes, each determined by network elasticity; but can be stored in temporary shapes by material immobilization, commonly by vitrification or crystallization.³⁰

As a simple example, a complex three-dimensional shape memory polymer shape can be compacted into a slender form (suitable for catheter delivery to the body or to fit into an otherwise compact space) by a cycle of heating, deforming, cooling, and unloading. Later, application of heat, light, or solvent exposure can trigger a return to the equilibrium complex shape through network chain mobilization. Most engineers and scientist will immediately recognize the practical applications possible with a polymeric material able to exhibit such a shape memory effect. However, this deceptively simple shape memory effect is achieved only through a large understanding of polymer chemistry and physics.

A. Shape Memory Polymer History

Shape memory polymers have only been around for about three decades. One of the first papers to address shape memory polymer was written by Y. Shirai, S. Hayashi in 1988.³¹ Shape memory polymers are thought to have applications from deploying objects in space to manufacturing dynamic molds. Unlike shape memory alloys, shape memory polymers exhibit a radical change from a normal rigid polymer to very stretchy elastic and back on command, a change which, in theory, can be repeated without degradation of the material. The "memory," or recovery, quality comes from the stored mechanical energy attained during the reconfiguration and cooling of the material.

The first industrial applications of the shape memory effect occurred in the 1950s when chemist Paul Cook, founder of Raychem Corporation, invented heat shrink tubings using radiation-cross-linked polyethylenes³². The term "shape memory polymer" became better known as shape memory poly(norborene), which was developed by the French company CDF-Chimie, and was commercialized in Japan by Nippon Zeon Company in the 1980s under the brand name Norsorex.³³ Poly(trans-isoprene) and poly(styrene-butadiene) with shape memory effect were subsequently developed by two other Japanese companies³⁴.

These events ushered in a government and corporate sponsored rush of shape memory polymer research, which primarily focused on polyene-

based systems until segmental polyurethane-based shape memory polymers were introduced by Mitsubishi Heavy Industry (MHI) in the early 1990s.³⁵ The flexibility of urethane chemistries enabled the development of shape memory polyurethanes with a wide range of mechanical properties and glass transition temperatures (T_g 's) for individual applications. The publication of a series of papers by Lendlein et al. beginning in 2002, exploring the potential application of shape memory polymers in modern medicine, ushered in another surge in shape memory polymer research. Since then, over one hundred shape memory polymer-related patents and research articles are published annually³⁶.

All of this research focused attention on developing new material systems with more tightly defined and narrow transition temperature ranges. As will be discussed further, transition temperatures are even more important in shape memory polymers than SMAs due to the complex range of temperatures possible with shape memory polymers and the nature of the polymeric materials from which they are made.

Above its transition temperature, shape memory polymer goes from a rigid, plastic state to a flexible, elastic state. When cooled, it becomes rigid again and can be constrained in its new shape configuration.³⁷ Shape memory characteristics can be engineered into most polymers.³⁸ Some of current shape memory polymer formulations are based on styrene

and acrylates, cyanate ester, maleimides, and epoxy polymer systems and will be covered in more detail later in this paper.

The shape memory effect is not a universal property of all polymeric materials.³⁹ In order to have a shape memory effect the polymer networks must comprise reversible switching components, which are responsible for maintaining the dimensional stability and determining reversible thermal response of the polymer. These networks merely have the potential to be programmed to exhibit shape memory effect. Processing histories and programming conditions also impact the shape memory effect of a shape memory polymer. The intrinsic mechanism for shape memory behavior in thermal responsive shape memory polymers is the reversible freezing and activation of polymeric chain motion in the switching segments below and above the transition temperature, respectively.⁴⁰ Shape memory properties have been reported in a wide range of polymers including, but not limited to, polyurethanes, epoxies, polyolefins and polyesters.⁴¹

B. Shape Memory Polymer Basics

A polymer engineered with shape memory characteristics provides a unique set of material qualities and capabilities that enhance the traits inherent in the polymer system itself. Shape memory polymers normally change between rigid and elastic states by way of thermal stimuli. Other stimuli are possible and will be discussed later, but for ease of

discussion, thermal stimuli is assumed to be used. The change in states takes place at what is referred to as the glass transition temperature (T_g). Shape memory polymer can be formulated with a T_g that matches an applications need. Current shape memory polymer systems have been demonstrated with T_g s from -30°C to 260°C (-22°F to 500°F).⁴²

1. The Basic Shape Memory Polymer Cycle

The evolution of stress (or force), strain, and temperature during a thermo mechanical cycling of an SMP is referred to as the shape memory cycle. An SMP will typically start as a semicrystalline network polymer. Initially, at a temperature higher than the SMP transition temperature, at which the material exists in a rubbery, elastic state, the material is deformed to a certain strain. Subsequent cooling under constant stress (or strain) to a temperature lower than the transition temperature causes the material to adopt a more rigid state, in this case the semi-crystalline state, therein immobilizing the constituent polymer chains and allowing fixing or freezing of the deformation as latent strain energy. The shape recovery is achieved by heating the material without any stress to a temperature generally greater than the transition temperature. The stored strain energy is then released owing to the regained chain mobility.

The primary driving force for shape recovery is entropic in nature; it is energetically favorable for the material to return to its most disordered

conformation.⁴³The abilities of SMPs to fix a temporary shape and to recover an original shape in a controlled fashion through use of external stimuli (i.e., heat, electric field, magnetic field, and irradiation) distinguish them from most conventional polymeric materials. Shape fixing and shape recovery reflect the various microstructural transformations and determine the extent to which SMPs can be practically used, and therefore, are of both fundamental and practical importance.

In its permanent, or memorized macroscopic shape, the molecular chains of an SMP adopt conformations with the highest entropy, that is, the chains are in a thermodynamically stable state. Upon heating above the T_g , the chain mobility is significantly activated. When an external deformation load is applied, the chain conformations are changed leading to a lower entropy state and macroscopic shape change. When the SMP is cooled below T_g , this lower entropy state (or the temporary shape) is kinetically trapped due to the freezing of the molecular chain segments, resulting in the macroscopic shape fixation. Upon reheating above T_g under a stress free condition, the molecular mobility is re-activated, which allows the chains to return to their highest entropy state (i.e. recovery of the permanent shape). This change likely depends on the molecular structure of the SMP.⁴⁴

Figure 4 shows a complete thermomechanical cycle example of a shape memory polymer (SMP), cross-linked poly(cyclooctene), as a plot of

temperature versus strain and stress. A heated, unloaded sample (asterisk or state iv) is deformed to state i and cooled through a fixing temperature to state ii, followed by unloading (revealing the degree of strain fixing) to state iii, and finally by unloading to the original state (iv) if the strain recovery is complete. Three consecutive cycles are shown, revealing excellent repeatability. Above its transition temperature, shape memory polymer goes from a rigid, plastic state to a flexible, elastic state. When cooled below that temperature, it becomes rigid again, with high specific strength. The shape memory polymer can be manipulated and cooled into a variety of new shapes; when heated above its transition temperature, it will return to its "memorized" shape.⁴⁵

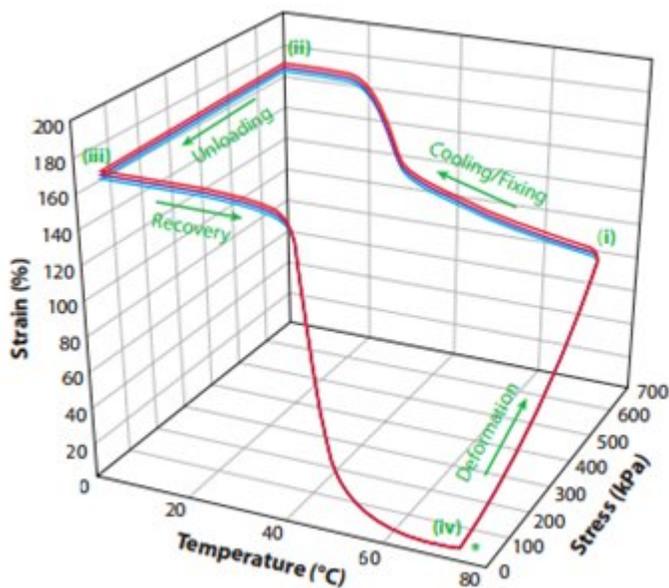


Figure 4 A complete thermomechanical cycle for an SMP.

What is not specifically designated in Figure 4 is the transition temperature. Figure 5 is a plot of the elastic modulus versus temperature, typically found from testing via dynamic mechanical analysis (DMA). Shape memory polymers are characterized by triggering segments that have a specific T_g . As previously discussed, at a temperature above T_g , the material can be easily deformed, i.e. it has a low elastic modulus. The deformed shape can be maintained when the material is cooled below the T_g . The material will "remember" or return to its original shape when it is heated to a temperature above the T_g again.

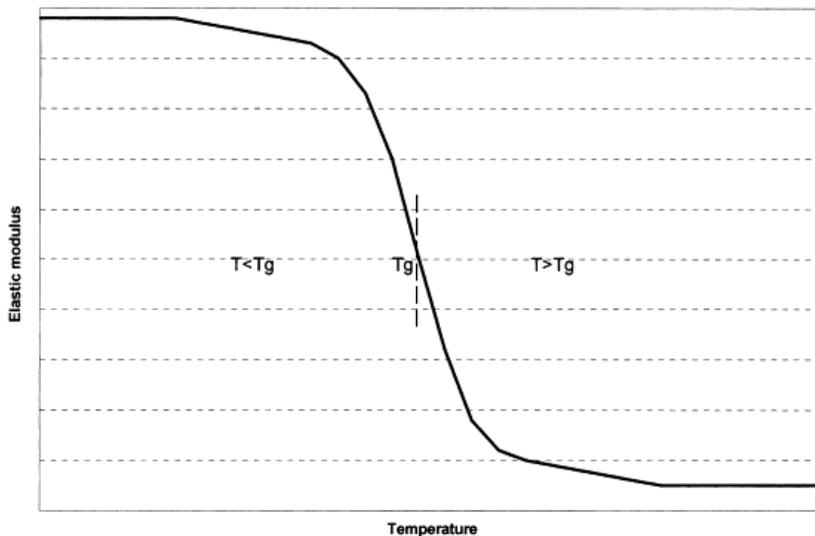


Figure 5. Representative plot of Temperature versus Elastic Modulus

Regardless of the molecular structures, whether or not a polymer is an SMP can be determined from its DMA curve. Ideally, an SMP upon heating should have at least a two to three orders of magnitude drop in the elastic modulus, but the modulus should quickly reach a plateau value after such a drop, as seen in Figure 5. These two DMA features are and will continue to be the most important guidelines in designing SMPs.

From the molecular dynamics standpoint, the modulus drop is indicative of the significant activation of molecular mobility at the multi-segmental scales. The rubbery plateau, on the other hand, arises from the prohibition of chain slippage at a longer length scale (e.g. the entire polymer chains slip past one another). Thus a glass transition or melting transition offers the mechanism for controlling the molecular mobility, whereas the crosslinking is responsible for the prohibition of the long-range chain slippage.⁴⁶

Two other values that can be used to describe shape-memory effects are the strain recovery rate (R_r) and strain fixity rate (R_f) and can be calculated by equations 1 and 2 below. The strain recovery rate describes the ability of the material to memorize its permanent shape, while the strain fixity rate describes the ability of switching segments to fix the mechanical deformation.

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \quad (1)$$

$$R_f(N) = 1 - \frac{E_f}{E_g} \quad (2)$$

Equations one and two are used to describe the R_r and R_f where N is the cycle number, ε_m is the maximum strain imposed on the material, and $\varepsilon_p(N)$ and $\varepsilon_p(N-1)$ are the strains of the sample in two successive cycles in the stress-free state before a yield stress is applied.⁴⁷

While in its elastic state, shape memory polymers will recover its cast, or cured, shape if left unrestrained. Otherwise, they may be reconfigured or manipulated into other shapes, tolerating between 100% to 600% elongation with the percent of elongation dependent on the polymer chemistry. When a shape memory polymer is heated above its transition temperature it can be stretched, folded, rolled, twisted, or bent. At any point, the shape memory polymer can be cooled to maintain its altered shape indefinitely. Once it is brought above its transition temperature the shape memory polymer recovers its "memorized" shape very quickly.

2. So What is a Shape Memory Polymer?

A shape memory polymer is not simply an elastomer, nor simply a plastic. It exhibits characteristics of both materials, depending on its temperature. It also has properties like a thermoset and thermoplastic polymer. While rigid, it demonstrates the strength-to-weight ratio of a rigid polymer. While pliable, it has the flexibility of a high-quality, dynamic elastomer. While elastic, a shape memory polymer can be manipulated in many ways. It can be reshaped many times without losing material integrity.

A shape memory polymer can be cast and cured into any "memorized" shape, from a thick sheet to a concave dish, to a complicated open honeycomb network. A shape memory polymer can also be used as a coating on another material. This versatility would make shape memory polymers ideal for applications such as dynamic configurable parts, deployable components, and inexpensive, reusable custom molds if the price and production speed would make a viable business.

The shape memory polymer effect can be interpreted as a thermo-mechanically programmed effect originated from the viscoelasticity intrinsic to polymers. This is in sharp contrast to SMAs, which can only be expected for a limited numbers of metallic alloys with certain compositions. Despite the fact that a typical SMP exhibits much lower recovery stress and slow actuation compared to SMAs, SMPs do hold a number of advantages over SMAs in processability, maximum recoverable strain, and easily tunable shape memory characteristics.

Given the nature of the shape memory effect for polymers, a key aspect of the SMP research lies in the creation of innovative ways to take advantages of the polymeric shape memory properties to achieve practical benefits. On the other hand, any given application may require SMPs with specific characteristics such as the shape memory transition temperature, maximum recoverable strain, and recovery stress. This can be conveniently achieved via chemical composition and process tuning for SMPs.⁴⁸

C. Shape Memory Polymer Composites

No review of shape memory polymer would be complete without a discussion of their use in composites. Shape memory polymer resin is an integral component of a shape memory composite system. A shape memory composite acquires some shape memory polymer characteristics, making it a unique material for use in structures and other applications requiring both load strength and "shape-shifting" flexibility.

Under thermal controls, shape memory composites can be temporarily softened, reshaped, and rapidly hardened to function as structures in a variety of configurations. An example of a use for this versatility is the capability for space-efficient stowing, and then later deployment to the operational shape. The composites can be fabricated with nearly any fiber type, and creative reinforcements permit dramatic shape changes in functional structures. Shape memory composites are also

machinable. Their use is slowly growing, and in many cases, is preferred over the use of pure shape memory polymer because of the increased toughness, strength and processing capability that a composite has but will continue to be limited until pricing and production are improved.

III. Types of shape memory polymers and Activation Methods

Generally, shape memory polymers are comprised of two essential components; the back bone polymer, which is comprised of monomeric constituents that undergo polymerization to produce polymers possessing specific glass transition temperatures (T_g s), and a crosslinking agent. The mixture of monomers can be formulated so that the glass transition temperatures can be tuned to meet different operational needs for specific applications. However, the exact chemistry to introduce this crosslinking into the material varies with different polymers.

A. Polyurethanes

Probably the best known and best researched polymer type exhibiting shape memory polymer properties is polyurethane polymers. Gordon and Tobushi exemplify studies directed to properties and application of shape memory polyurethanes.⁴⁹ The flexibility of urethane chemistries enabled the development of shape memory polyurethanes with a wide range of mechanical properties and glass transition temperatures (T_g 's) for individual applications.

1. Chemistry

An example of one system is disclosed in the European Patent EP0363919 A2.⁵⁰In this system, the first raw material is a difunctional isocyanate which is represented by the general formula OCN--R--NCO , where R is a group having none or one or two benzene rings. It includes, for example, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, carbodiimide-modified 4,4'-diphenylmethane diisocyanate, and hexamethylenediisocyanate.

The second raw material for this system is a difunctional polyol which is represented by the general formula OH--R'--OH , where R' is a group having no or one or two benzene rings. The second raw material may also be a reaction product of a difunctional polyol and a difunctional carboxylic acid or cyclic ether. This group can include polypropylene glycol, 1,4-butane glycol adipate, polytetramethylene glycol, polyethylene glycol, and an adduct of bisphenol-A with propylene oxide.

The third raw material is a difunctional chain extender containing active hydrogen which is represented by the general formula OH--R''--OH , where R'' is a $(\text{CH}_2)_n$ group or a groups having one or two benzene rings. It includes, for example, ethylene glycol, 1,4-butane glycol, bis(2-hydroxyethyl)hydroquinone, an adduct of bisphenol-A with ethylene oxide, and an adduct of bisphenol-A with propylene oxide.

2. Processing

As discussed above, the shape memory effect is not automatic. Special processing is needed to achieve the desired result. Therefore, the above-mentioned three raw materials (isocyanate, polyol, and chain extender) are made into a urethane elastomer (by the aid of an optional catalyst) by prepolymer process in the following manner. First, the diisocyanate and polyol are reacted in a specific molar ratio of $[NCO]/[OH]$ to give a prepolymer. When the reaction is complete, the chain extender is added in an amount sufficient to establish a desired molar ratio of the $[chain\ extender]/[prepolymer]$.⁵¹ After defoaming, the resulting mixture is poured into a mold, followed by curing to facilitate a crosslinking reaction at 80°C for one or two days in a constant temperature dryer. This process may be carried out with or without solvent.

3. Structure

The polyurethane elastomer produced as mentioned above will have a T_g and other physical properties as desired, if the following six factors are properly selected. (1) the kind of the isocyanate, (2) the kind of the polyol, (3) the kind of the chain extender, (4) the $[NCO]/[OH]$ molar ratio, (5) the $[chain\ extender]/[prepolymer]$ molar ratio, and (6) the curing condition. Since this is a copolymer, the final T_g will depend on the amount, type and ratios of the polymers used to make it and the amount of crosslinking.

The thus produced polyurethane elastomer may be represented by the following general formula:



where m is 1-16 and n is 0-16.⁵²

This process has changed very little in the years since its publication.⁵³ Certain refinements have been made, but the overall chemistry has remained the same. The importance of tuning the properties of the shape memory material through the careful selection of monomers and amounts of agents is not reduced by the

B. Epoxy Systems

While polyurethanes have the ability to meet many biomedical requirements, they cannot meet other needs. In the last twelve years other chemistries and processing techniques have been created to utilize the shape memory effect. One such chemistry is based on the common epoxy polymer.

1. Chemistry

Most epoxy shape memory polymer systems are a reaction product of at least one reagent containing two active amino-hydrogen or two active phenolic-hydrogen which is reacted with at least one multifunctional cross linking reagent which contains at least three or more active amino- or phenolic-hydrogen or is a reagent containing at least three glycidyl ether moieties. This combination is then further mixed with at least one diglycidyl ether reagent. The resulting mixture is cured and has a glass transition temperature higher than 0°C. This reaction creates crosslinking between the monomers and polymers such that during

polymerization they form a cross-linked thermoset network. One such system is disclosed in U.S. Pat. No. 8,101,689.

In the case of epoxy shape memory polymer, this can be achieved by using amine and phenol reagents that form linear polymer chain with the diepoxide (e.g. Bisphenol A diglycidyl ether, which is the most commonly available epoxy resin) and cured with small amount of crosslinking multifunctional amine, phenol or glycidyl ether reagents. In contrast, common epoxy resins are normally cured with stoichiometric amount of diamine crosslinking reagents. The use of these amine reagents ensures there is enough flexibility between the crosslinking points within the polymer materials, and this flexibility or mobility is what imparts the materials with shape memory properties.

For epoxy shape memory polymers the crosslink density is crucial in controlling the elongation and transition temperature. For most applications using normal epoxy resin, the highest crosslink density possible is desired in order to maximize the T_g and thereby the use of the material. However, in shape memory polymers a relatively low crosslink density is required to allow movement of the epoxy chains, thereby increasing elongation and shape memory properties. If too few crosslinkers are present, the material behaves as a thermoplastic, irreversibly deforming at elevated temperatures. Thus care must be taken to find

the optimum crosslink density that allows for maximum elongation with full retention of original form.

Most publications discussing shape memory polymer define crosslink density as the number of moles of crosslinker divided by the total moles of the resin system. In formulation, balanced stoichiometry must be used, meaning that all reactive epoxide groups must have one active amino-hydrogen or phenolic-hydrogen to react with. Therefore, the monomers containing two active amino-hydrogen or phenolic-hydrogen serve as chain extenders while the multifunctional- amines, phenols, or glycidyl ethers serve as crosslinkers. In formulation, two equations must be solved simultaneously: one balancing all reactive groups and the other defining the crosslink density. Depending on the curing agents and epoxies used, crosslink densities ranging from 0.2 mol% to 10 mol% based on total number of moles.

2. Processing

Dissolving thermoplastics in epoxy resins is often performed to increase toughness. Often, solvents or kneading machines are used to adequately blend thermoplastics and epoxy resins. One approach that can be taken with epoxy shape memory polymer is in situ polymerization, where a thermoplastic modifier is polymerized during the cure of the epoxy resin. The thermoplastic polymerizes via a free-radical addition mechanism, while the epoxy polymerizes in an epoxide ring-opening reaction. This allows simple mixing of the two low viscosity resins:

the thermoplastic monomers and the epoxy resin system. The T_g of the original epoxy formulation is affected depending on the thermoplastic used and degree of polymerization. Styrene and acrylate monomers can be used together and independently to tailor the T_g of the material. The loading of initiator can also be modified to control the chain length of the thermoplastic molecules. The presence of the thermoplastic phase does not hinder the elongation of the epoxy matrix. Any loading is possible, although visible phase separation occurs above 10 weight percent for polystyrene systems.

In addition it is possible to tune the mechanical properties such as toughness and T_g of the epoxy shape memory polymer using thermoplastic polymers. Thermoplastics are dissolved in epoxy resin systems to increase toughness, enhance self-healing properties, and modify other material properties. By incorporating thermoplastics in epoxy shape memory polymer resin the mechanical and chemical properties of the final shape memory polymer can be tailored to specific design and environmental requirements.⁵⁴

3. Structure

One of the general forms of epoxy shape memory polymers is:

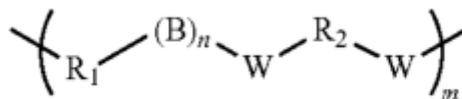


Figure 6 General Structure of Epoxy SMP

Where B has the structure:

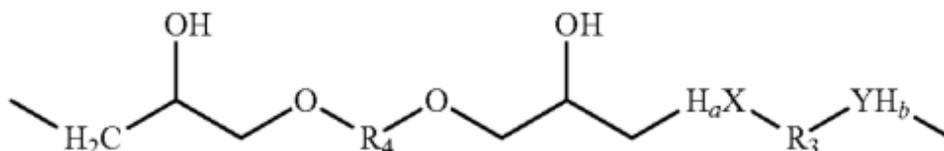


Figure 7 One of the functional groups of Epoxy ESMP

And where W has the structure:

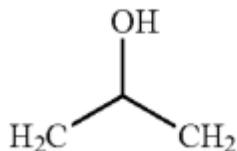


Figure 8 The second functional group in Epoxy SMP

and wherein R_1 is a tri-functional, tetra-functional or penta-functional amine or aromatic ether moiety and may be the same or different between each group, and wherein R_2 , R_3 , and R_4 , may be any aliphatic or aromatic monomeric unit or polymer and may be the same or different between or amongst each group, and wherein X and Y can be N or O and can be the same or different between or amongst each group, and wherein a and b can be 1 or 2, and wherein n and m can

be any positive non-zero whole number. Other forms are possible depending on what the desired application is.⁵⁵

C. Maleimide Shape Memory

Another new chemistry system was published in 2007 based on maleimide chemistry. This system of shape memory polymers has high glass transition temperatures as compared to other shape memory polymers. This polymer system would likely be particularly useful in the making of molds for composite manufacturing and in high performance structural components that require shape change capability. These new materials allow the needed elevated temperatures to be reached inside the mold to cure the resin part without exhibiting deformation of the mold itself. One such system is disclosed in U.S. Pat. No. 7276195.⁵⁶

1. Chemistry

Similar to all shape memory polymers, the maleimide system is a copolymer formed from a reaction of two monomers. The first monomer is selected from the category of maleimide-based monomers, and the second monomer is a vinyl monomer. The polymerization reaction forms castable shape memory polymers with glass transition temperatures higher than 100°C. The reaction also includes addition of a multifunctional crosslinking agent into the polymerization reaction so that the copolymer is cross-linked during polymerization to form a thermoset network.

In addition to the two noted monomers and the multifunctional crosslinking agent, an initiator such as an organic peroxide compound is also present. The transition temperatures of the final polymers are adjusted by the ratio of the monomers selected so that the resulting polymer has a T_g of from about 150°C to about 270° C. while the degree of crosslinking controls the rubbery modulus plateau.

These new copolymers are prepared from a reaction mixture which includes, in addition to maleimide-based monomer and the vinyl compound, a crosslinking agent and an initiator. By careful preparation of the reaction mixture the glass transition temperature, T_g of the resulting shape memory polymer can be synthesized to match the operating temperature of the composite manufacturing process and morphing structures.

One example of this reaction mixture is described in detail below. The first monomer can be either an N-arylmaleimide, such as N-phenylmaleimide or and N-alkylmaleimide, such as N-ethylmaleimide. The second monomer is a vinyl compound other than maleimide.

The crosslinking agent is a multifunctional compound compatible with the system chemistry. Thus, the crosslinking agent is a compound that has a polymerizable functionality of at least 2. The initiator of the reaction mixture may be any of the well-known initiators such as a free radical or an ionic initiator. Also, ultraviolet and gamma irradiation can be used.

This compound was one of the first to mention a specific optional component that was a modifying polymer. The modifying polymer acts as a viscosity adjustor and, additionally provides the requisite toughness to the resultant shape memory polymer. The modifying polymer is typically a thermoplastic polymer that is compatible with the polymer formed by the reaction product of styrene and a vinyl compound. When the optional modifying polymer is used, the resulting reaction product includes two distinct polymers, namely the SMP polymer and the "modifying" polymer.

The constituents of the shape memory polymer reaction mixture are present such that the maleimide monomer constituent represents between about 30% to about 99%, the vinyl monomer (other than maleimide) constitutes between about 0% and about 60%, the crosslinking agent constitutes between about 0.5% and about 5%, the initiator is present in a concentration in the range of between about 0.1% and about 4% and the modifying polymer, if present, represents between about 0.5% and about 60%, all of the above recited percentages being by weight based on the total weight of the shape memory polymer reaction mixture (100 wt %).

2. Process

The shape memory polymer reaction mixture is polymerized by reacting the mixture at a temperature in the range between 20°C and about 200°C, and a pressure in the range about 14.7 psi and about 50 psi over a time period in

the range about 2 seconds to 4 days to produce a cross-linked shape memory polymer. In addition, the shape memory polymer reaction mixture can be polymerized by the application of ultraviolet light or visible light with the presence of a photoinitiator or by the application of high energy electron beam radiation.

The shape memory phenomenon in the vicinity of T_g and the ability to set the value of T_g by varying the composition over a very broad range of temperatures allows contemplation of numerous applications in varied uses when thermoreversibility of a geometric shape is the desired aim.

3. Structure

In accordance with the aboveprocess description, the shape memory polymer developed with the process is prepared from a maleimide monomer (a) having the structure

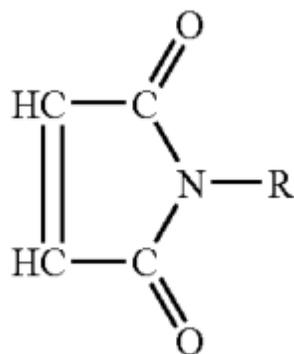


Figure 9 General Structure of Styrene SMP

wherein R is H, C₁-C₁₂ alkyl or aryl. Preferred alkyl substitutes for R are the lower (C₁-C₄ alkyl) moieties. This polymer has a glass transition temperature of about greater than about 100°C, preferably greater than about 150°C. As per the above, the polymer exists in the form of a cross-linked thermoset network. Presently, it is preferred that the maleimide monomer, monomer (a), be present in an amount of 1-12 mols per mol of the second vinyl monomer, monomer (b). Preferably, the maleimide monomer is N-phenylmaleimide. Glass transition temperatures for the resulting SMP polymer of about 180°C to 270°C are most preferred and achieved in accordance with the invention when the second monomer, monomer (b), is styrene in varying molar amounts relative to monomer (a).

D. Acrylates and Styrene Based

One of the first commercially developed shape memory polymers was based on acrylate chemistry. This was soon followed by a styrene-acrylate copolymer chemistry.

1. Chemistry

Acrylates and Styrenes are another widely studied polymer system that was developed in 2000.⁵⁷ These shape memory polymers include norbornene homopolymers and copolymers of norbornene and alkylated, cyano,

alkoxylated, mono- or diesterified imides or carboxylic acid derivatives may be employed. In addition, the copolymer may include, as a co-monomer, dimethanooctahydronaphthalene (DMON). Alternatively, homopolymers of DMON, and well as copolymers of DMON and styrene, acenaphthalene or dicyclopentadiene, which may be hydrogenated or halogenated, may be employed. By creating a copolymer of styrene and a vinyl compound other than styrene a styrene-acrylate based copolymer can exhibit the shape memory effect.

1. Chemistry

One example of this type of shape memory polymer is disclosed in U.S. Pat. No. 6759481. This copolymer is prepared from a reaction mixture which includes, in addition to styrene and the vinyl compound, a crosslinking agent and an initiator. Indeed, by careful preparation of the reaction mixture the glass transition temperature, T_g of the resulting shape memory polymer can be synthesized to match the operating temperature of the contact lens manufacturing process.

In a preferred embodiment of the present invention, the reaction mixture includes, in addition to the first monomer, which is styrene, the second monomer, which is a vinyl compound other than styrene, the crosslinking agent, which is a multifunctional compound, and an initiator, a fifth component, a modifying polymer. The crosslinking agent of the shape memory polymer reaction mixture is

multifunctional, that is, the crosslinking agent is a compound has a polymerizable functionality of at least 2.

The initiator of the reaction mixture may be a free radical or an ionic initiator. Free radical initiators within the scope of the present invention include organic peroxides and azo compounds. The ionic initiators are preferably cationic initiators.

As stated above, the SMP reaction mixture may include a fifth, optional component. This fifth component of the shape memory polymer reaction mixture is optional. That optional component is a modifying polymer. The modifying polymer acts as a viscosity adjustor and, additionally provides the requisite toughness to the resultant shape memory polymer. The modifying polymer of the shape memory polymer reaction mixture is a thermoplastic polymer that is compatible with the polymer formed by the reaction product of styrene and a vinyl compound.

2. Processing

The constituents of the shape memory polymer reaction mixture are present such that the styrene monomer constituent represents between about 30% to about 95%, the vinyl monomer constitutes between about 5% and about 60%, the crosslinking agent constitutes between about 0.5% and about 5%, the initiator is present in a concentration in the range of between about 0.1% and about 4% and the modifying polymer, if present, represents between about 0.5% and about

60%, all of the above recited percentages being by weight based on the total weight of the shape memory polymer reaction mixture.

The modifying polymer of the shape memory polymer reaction mixture is a thermoplastic polymer that is compatible with the polymer formed by the reaction product of styrene and a vinyl compound. Potentially compatible polymers include olefin polymers and styrene polymers. Other compatible polymers include polystyrene, poly(styrene-co-butadiene), polyethylene and polypropylene.

The shape memory polymer mixture is polymerized by reacting the mixture at a temperature in the range between 20°C and about 150°C. and a pressure in the range between 14.7 psi and about 50 psi over a time period in the range from 2 seconds and 4 days to produce a cross-linked shape memory polymer.

E. Activation Mechanisms

There are many activation methods for thermally responsive shape memory polymer: resistive heating; embedded heaters (for example, stretchy heaters, nichrome wires); contact heating; Induction heating; Dielectric heating; Microwave heating; Infrared radiant heating; Light; Electromagnetic Radiation; and Magnetism are just a few that have been documented.⁵⁸

Determining the properties of SMP is typically done by direct heating in highly controllable temperature environments such as an oven or a DMA machine. Access to direct heating may not be realistic for technological implementations of SMP devices. To fully integrate SMP into the marketplace, alternative recovery triggering methods have been one of the major focus areas of SMP research. Notably, infrared radiation and magnetic induction heating have emerged as attractive methods owing to their remote heating nature. Non-remote but indirect heating methods such as resistive heating has also been proven attractive due to its high speed.

Non-heating based light activated SMP systems have also been explored. Lendlein et al. demonstrated an SMP for which the shape fixing and recovery were enabled by actively changing the crosslinking density via photo-reversible cinnamate chemistry.⁵⁹ This chemistry is also the subject of numerous patents.⁶⁰ Practical issues for the cinnamate based light activated SMP range from limited shape fixity, slow activation, to limited light penetration into the SMP bulk. Nevertheless, light activation of SMP has drawn attention due to its mechanistic uniqueness. Very recently, Lee et al. reported a light activated SMP system based on the photoisomerization of azo functionalities in a glassy liquid crystalline network.⁶¹ A short exposure to eye-safe linearly polarized 442 nm light allowed a deformed shape to be fixed and the recovery was triggered by exposure to circularly polarized light of the same wavelength. This was

surprising as most light activated systems before required different wavelengths for the activation and shape fixation steps.

Besides the mechanical difference between heat and light activations, the latter offers a unique benefit in that light can be controlled to activate only a portion of the shape memory polymer material. The feature will lead to discrete activation and products which are not possible with heat activation.

Another mode of triggering mechanism is based on the absorption of water, which induces recovery by reducing the T_g through the plasticization by water instead of heating.⁶² This mode of recovery triggering cannot be universally applied, but it is quite relevant for shape memory polymer applications in which water is present in the environment, as is the case for biomedical-implanted devices.

Other activation methods are not well defined or understood at this point. The principles of induction heating with magnetic particles are well understood, however, there has not been enough research into the use of them as a practical heating method.⁶³ Additionally, other electromagnetic wave activation, in addition to infra-red, ultraviolet, and visible light is currently in the beginning stages of research.

IV. Coming Future Developments

There is plenty of work still to do to make shape memory polymers a commercially viable product. This paper will examine the two main avenues of research believed to be necessary to make shape memory polymers viable.

A. Three Way Shape Memory

A paper was published in 2006 that showed two distinct thermal transitions in a cross-linked network can be independently utilized to fix and recover two temporary shapes, all in one shape memory cycle.⁶⁴ This is called the triple-shape memory effect (triple-SME), indicative of a total of three shapes involved, including the permanent shape. The triple-SME represents an extension of the traditional fully reversible shape memory effect, which relies on one thermal transition for one temporary shape. The significance of the triple-SME has the potential to revolutionize the use of shape memory polymers.

The triple-SME and the quantitative triple-shape cycle are illustrated in Fig. 8 for a cross-linked polymer with two distinctive T_g s at 38°C and 75°C.⁶⁵ Relative to the dual-shape cycle which has one shape fixing and one shape recovery step (Fig.

4), a triple-shape cycle comprises of two shape-fixing steps and two shaperecovery steps.

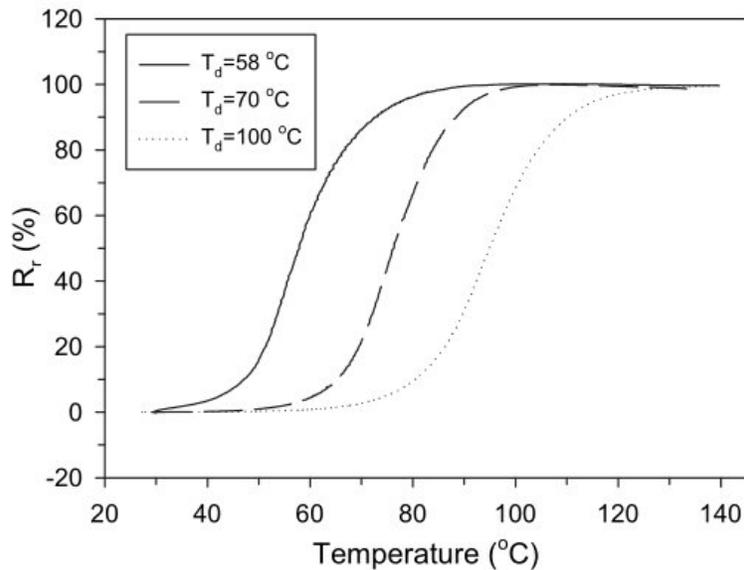


Figure 10 A Temperature vs. Rr plot for a three way SMP

In the two-step shape fixing process, the permanent shape A was first heated to a temperature above both T_g s and deformed by imposing a first stress. The material was then cooled under this stress to a temperature between the two T_g s and releasing the stress. This fixed a first temporary shape. In the second fixing step, the first temporary shape was further deformed by imposing a second stress that was different from the first stress. This stress was maintained while the sample is cooled below both T_g s. Removal of the second stress after cooling led to a second temporary shape. Shape recovery is conducted under a stress free condition.

Heating of shape the material to a point between the T_{gs} recovers the first temporary shape. Further heating of the material above both T_{gs} leads to a recovery of the memory shape. The respective shape fixity (R_f) and shape recovery (R_r) can be calculated from equations one and two.

Alternative triple-shape procedures and materials have been reported in the literature. Instead of following the standard two-step shape fixing discussed above, a one-step shape fixing at a temperature higher than both T_g also been explored.⁶⁶ The one-step shape fixing may also be conducted at a temperature lower than both T_g (i.e. cold drawing one-step shape fixing). Regardless of the difference in the shape fixing process, the triple-SME is qualified if two distinct steps are present in the later recovery event. The one step shape fixing procedures represent simpler ways for realization of triple-SME. However, they cannot be used when two independent strains are to be programmed into the shape memory polymer. In addition the one step shape fixing procedures yield only an overall shape fixity and are unsuitable for independent evaluation of shape fixing capabilities of the two transition phases.

As for shape recovery, the main variation lies in the heating method. The two-step recovery may be triggered by continuous heating to a temperature above both T_{gs} , typically at a low linear ramping rate. The distinction in the heating method is non-trivial. It is important to note that the coexistence of two

thermal transitions in a single polymer is not uncommon. For instance, semicrystalline polymers typically possess an amorphous phase (thus a glass transition) in addition to their crystalline phase. If cross-linked, they are expected to possess triple-shape behaviors.

The triple-shape memory polymer systems by Bellin were obtained by photopolymerizing a mono-methacrylate and a poly(ϵ -caprolactone)dimethacrylate (PCLDMA) macro-crosslinker.⁶⁷ In such systems, the PCLDMA macro-crosslinker provides a melting transition of 50°C while a second transition is determined by the choice of the mono-methacrylate. When a poly(ethylene glycol) (PEG) containing mono-methacrylate was used as the monomer, the second transition was the melting transition associated with the PEG chain. When cyclohexylmethacrylate was employed instead, the second transition arose from the glass transition of the poly(cyclohexyl methacrylate), which is 140°C. Such an approach is highly versatile. The choice of the monomers and crosslinkers allows adjusting the two transition temperatures independently, whereas the variation in monomer ratio changes the relative fractions of the two phases.

Others have demonstrated that the combination of the glass transition and the liquid crystalline transition can also be utilized to realize the triple-shape function.⁶⁸ This liquid crystalline system shares, in principle, similar versatility to

Bellin et al.'s system in terms of tunability. The limitation lies in the synthetic access to various liquid crystalline monomers of different liquid crystalline transition temperatures.

Polyurethane chemistry has also been explored in the synthesis of triple-shape memory polymer. Star-shaped hydroxy-telechelic poly(pentadecalactone) (PPD) and poly(ϵ -caprolactone) (PCL) precursors were cross-linked with a low-molecular weight diisocyanate, yielding a thermoset polymer network with two crystalline phases from the PPD and PCL, respectively.⁶⁹ The resulting polymers exhibit triple-SME following various shape fixing protocols, including standard two-step shape fixing, one-step shape fixing, and cold drawing one-step shape fixing.

Similarly, thermoplastic polyurethane triple-shape memory polymers have also been synthesized.⁷⁰ The reaction components include a diisocyanate and three diols (1,4-butanediol), poly(ϵ -caprolactone) diol ($T_m \approx 49^\circ\text{C}$), and poly(tetramethylene glycol) ($T_m \approx 23^\circ\text{C}$). The resulting multi-block poly-urethane contains one hard segment and two crystalline soft segments. The shape recovery behaviors of the resulting polymers were found to highly depend on the ratio between the two soft segments. Although detailed investigation of the triple-SME was not conducted, two-step shape recovery was illustrated for one of the polymers, indicative of the triple-SME. The melting temperature of polyethylene is highly

dependent on the degree of branching. By chemical crosslinking of a physical blend of linear and branched polyethylene, the multiple melting transitions in a resulting network can be explored for triple-shape functions, although it is not a certainty that the triple effect will be found.

The above triple-shape memory polymer systems represent macroscopically homogeneous polymer systems with the two thermal transitions originating from two micro-separated phases. A different approach to achieve triple-SME can be created by combining two epoxy-based dual-shape memory polymers of two well-separated transition temperatures in a macroscopic bilayer.⁷¹ In such a system, the two individual contributing layers are completely decoupled, allowing them to be independently tuned both in terms of their ratio and thermal transition temperatures. Fabrication of such a triple-shape memory polymer requires very little chemistry knowledge and skills due to the simplicity of the epoxy chemistry, which could be beneficial for non-chemists interested in building triple-shape memory polymer based devices. The interfacial strength between the two layers is crucial for triple-SME as large interfacial stresses are expected in the triple-shape cycle. If the interface is not sufficiently strong, delamination would have occurred and triple-shape behavior would not have been achieved.

For systems without a strong interface, the significant stresses encountered in the triple-shape cycle would lead to interfacial chain slippage that could compromise the triple-SME, in analogous to the delamination for the bilayer triple-shape memory polymer. In 2010, one publication reported the fabrication of triple-shape memory polymer composites by physical embedment of a non-woven thermoplastic nanofiber of poly(3-caprolactone) into a continuous cross-linked shape memory polymer matrix.⁷² Despite the reported lack of strong interactions (covalent or non-covalent) at the interface between the two contributing components, the triple-SME was also observed for the composite materials. Presumably, this suggests that robust physical confinement represents an alternative stress transfer mechanism effective for triple-SME. This composite approach is quite attractive in that the two contributing components in the composite material are decoupled. In principle, the concept could be expanded to a variety of material combinations with little chemistry constraint.

Although much progress has been made in terms of alternative recovery triggering mechanisms, the emergence of the multi-SME presents a new challenge. The two distinct recovery steps for the triple-SME, for instance, can only be realized through slow and finely controlled continuous temperature ramping or more practically two-stage heating. The profound impact of heating methods in achieving the triple-SME highlights the challenge of controlling heating in a practical setting encountered in potential applications. This issue is

particularly complicated for in vivo device applications, in which access to direct heating may be impossible.

B. Four Way

The emergence of the triple-SME invited a natural question: can multi-shape memory effect beyond triple be realized in a similar fashion by introducing additional discrete transitions? The answer is clearly yes.⁷³ But as previously discussed, the ultimate importance of the tunability of the T_g s and other properties is very important. In particular, tailoring T_g s has always been a major focus of research.

Traditionally, tuning has been achieved through material chemistry by altering the material chemical composition which leads to different transition temperatures. Obviously, this task becomes more and more challenging as more discrete transitions are needed for multi-SME. The fully reversible shape memory effect can be tuned without changes in its chemical composition, by the addition of modifiers or proper monomer selection. Tuning for multiple shape memory effect is possible. Of more importance than the multi-SME itself is the fact that the triple-SME, for instance, can be realized at any two arbitrary temperatures provided that they are sufficiently apart. This is in sharp contrast to more typical triple-SMPs, for which the fixing and recovery of the two temporary shapes only occur in the temperature windows defined by the two transitions. In essence, the tunable multi-SME allows a single material to perform

triple-shape memory functions that would normally be expected only for multiple triple-SMPs of different transition temperatures.

The basis of the tunable multi-SME is that a single broad thermal transition can be viewed as the continuous distribution of an infinite number of infinitely sharp transitions. Each of these sharp transitions can be further regarded as an elemental memory unit with a corresponding T_g . As such, only the elemental memory units with T_g below the deformation temperature are activated for the memory function. The continuously distributed nature of the elemental memory units ensures that any change in the deformation temperature within the broad transition would always correspond to a variable group of activated elemental memory units. The selection of the two deformation temperatures in a triple-shape memory polymer would activate two groups of elemental memory units that are variable depending on the deformation temperatures. The triple-SME is thus tunable via the selection of the deformation temperatures.

In contrast, the two distinct transitions for more typical triple-SMPs may be viewed as non-continuous distribution of two groups of elemental memory units within the two relatively narrow temperature windows. Accordingly, the deformation temperatures have to be either above or in between the two transition temperatures to activate two different groups of elemental memory units to enable the triple-SME. The two groups of elemental memory units are non-variable

unless the chemical composition of the polymer is changed, i.e., the triple-SME is thus non-tunable with the same polymer.

Bearing some similarity to the tunable multi-SMP is the functionally graded SMP.⁷⁴ Here a single piece of such an SMP possesses a linear spatial gradient in glass transition temperature, achieved by post-curing a pre-cured SMP in a linear temperature gradient. When a deformed functionally graded SMP is exposed to a continuous heating condition, the spatial gradient in T_g enables spatially sequential recoveries. Such a behavior is quite unique and represents a conceptually different approach to the multi-SME.

On the other hand, the graded SMP can be similarly viewed as the continuous distribution of primary memory units (PMUs) of different T_g s, albeit in a spatial manner. The broad thermal transition key to the tunable multi-SME has also been found responsible for the so-called temperature memory effect, which refers to the capability of an SMP system to memorize a temperature. Specifically, when an SMP is deformed at a temperature within its broad thermal transition and subsequently subjected to iso-strain stress recovery experiments, the maximum recovery stress would appear at a temperature identical to the deformation temperature. Essentially, the T_d can be recorded in the SMP. The associated phenomenon represents a drastic departure from the concept of SMP, which emphasizes solely the memory of shapes (or strains). The

temperature memory effect observed in the stress recovery experiments can be called the stress based temperature memory effect.

The practical benefit of the temperature memory effect lies in that, with the same polymer, the tuning of stress or strain recovery can be developed in a wide range and quantitatively predictive fashion. The fact that the tunable multi-shape and temperature memory effect rely both on the broad transition is not a coincidence. In fact, the concept of PMUs used to interpret the tunable multi-shape memory effect can be readily applied to explain the temperature memory effect. According to the concept, only the PMUs with T_g 's below the deformation temperature are activated for the strain fixing function. In the corresponding recovery event, 100% of PMUs are re-activated for recovery only when the temperature reaches the deformation temperature. Consequently, a peak recovery rate or peak recovery stress is observed.⁷⁵

V. Conclusion

The molecular origin of the shape memory polymer clearly suggests that the shape memory polymer should not be regarded as a property reserved to a small number of specially designed polymers. The properties of shape memory polymer are tunable through material selection, processing strategies, and modifying components. As the history of shape memory polymers has clearly indicated, the future prospect of shape memory polymers hinges heavily on how to best take advantages of the tunable nature of SMP and the shape memory effect.

On the positive front, the application potential for shape memory polymers appears almost unlimited as manifested in the highly diverse application concepts that have appeared in both peer-reviewed journals and patent literature. This is, however, in sharp contrast to the very few real world applications such as low value-added toys or cheap commercial products. This is also seen in that the majority of real uses of shape memory polymer are in the medical industry, which

is very expensive. The real key thus lies in the discovery of high value-added applications for which shape memory polymer are enablers or at minimum highly attractive alternatives.

Whereas biomedical applications of shape memory polymer represent a major focus for the shape memory polymer research today, stringent requirements and lengthy regulatory approval process present obstacles for commercial implementations. Under this scenario, whether or not any “silver bullets” beyond biomedical applications may emerge is an important issue.

Tailoring the characteristics of shape memory polymers to meet the specific requirements of targeted applications will continue to be an essential aspect of shape memory polymer research. The discovery of novel SMEs will play a significant role as it pushes the material capability into new territories and has the potential to impact the field in a more drastic fashion. Although it is impossible to predict what new polymer shape memory behaviors will be discovered in the future, several notable challenges and opportunities have been presented in this paper.

There is no one solution and it will likely take many more years, potentially decades, of research to determine the long term impact, usefulness, and viability of shape memory polymers in the mass consumer market. There is much promise, but there is also much work to be done. The novelty has worn off,

the fad has passed, and now we need to develop the materials to incorporate shape memory polymers into our daily lives.

REFERENCES

-
- ¹BilimAtli ; Farhan Gandhi ; Greg Karst; *Thermomechanical characterization of shape memory polymers; Journal of Intelligent Material Systems and Structures January 2009 20: 87-95*
- ²Wu, S; Wayman, C (1987). "Martensitic transformations and the shape-memory effect in Ti50Ni10Au40 and Ti50Au50 alloys". *Metallography* 20 (3): 359.; See also , K Otsuka, CM Wayman, *Shape Memory Materials*, Cambridge University Press, 1999
- ³*Id.*
- ⁴*Id.*
- ⁵*Id.*
- ⁶Reed-Hill R, Abbaschian R.; *Physical Metallurgy Principles, 3rd Edition*. Boston: PWS-Kent Publishing, 1991
- ⁷ Khan, Abdul Qadeer, *The effect of morphology on the strength of copper-based martensites*, March 1972,
- ⁸ *Id.*
- ⁹ Ashby, Michael F.; & David R. H. Jones; *Engineering Materials 2*, Oxford: Pergamon Press., 1992.
- ¹⁰ Bhadeshia, H. K. D. H.; *Geometry of Crystals*; London: Institute of Materials. 2001
- ¹¹ Dimitris C. Lagouda, editor; *Shape Memory Alloys: Modeling and Engineering Application*; Springer Science Busienses Media, 2008.
- ¹² *Id.*
- ¹³ *Id.*

-
- ¹⁴Pierre-Antoine Gédouin; ShabnamArbabChirani; Sylvain Calloc; *Phase proportioning in CuAlBe shape memory alloys during thermomechanical loadings using electric resistance variation*; International Journal of Plasticity; Volume 26, Issue 2, February 2010, Pages 258–272
- ¹⁵F. H. Herbstein; *On the mechanism of some first-order enantiotropic solid-state phase transitions: from Simon through Ubbelohde to MnyukhActaCryst.* ActaCryst. (2006). B62, 341-383.
- ¹⁶H.R. Chen, ed., *Shape Memory Alloys: Manufacture, Properties and Applications*, Nova Science Publishers Inc., 2010
- ¹⁷K. Rajagopal; *Engineering physics*; PHI Learning Private Limited, 2011
- ¹⁸XianghePeng, Bin Chen, Xiang Chen, Jun Wang, Huyi Wang; *A constitutive model for transformation, reorientation and plastic deformation of shape memory alloys*; ActaMechanicaSolidaSinicaVolume 25, Issue 3, June 2012, Pages 285–298
- ¹⁹Filip, P; *Influence of work hardening and heat treatment on the substructure and deformation behaviour of TiNi shape memory alloys*; ScriptaMetallurgica et Materialia 1995
- ²⁰Kauffman, George, and Isaac Mayo; *Memory Metal*; Chem Matters Oct. 1993: 4–7.
- ²¹K. Otsuka and C.M.Wayman; *Shape Memory Materials*; Cambridge University Press, 1999
- ²²Id.
- ²³Id.
- ²⁴Id.
- ²⁵Id.
- ²⁶Id.
- ²⁷Id.
- ²⁸Id.
- ²⁹SMA's however are very useful in the Medical field where biocompatibility is essential; See Generally LorenzaPetrini and Francesco Migliavacca; *Biomedical Applications of Shape Memory Alloys*; Journal of Metallurgy Volume 2011, 2011
- ³⁰Patrick T. Mather, XiaofanLuo, and Ingrid A. Rousseau; *Shape Memory Polymer Research; Annual Review of Materials Research*; Vol. 39: 445-471 August 2009
- ³¹S. Hayashi andY.Shirai, *Mitsubishi Techn. Bull. No. 184*, December 1988
- ³²Dole, M.; *History of the Irradiation Cross-Linking of Polyethylene*. Journal of Macromolecular Science-Chemistry Vol. 05, 1981
- ³³Reza Fazel-Rezai editor;*Biomedical Engineering - Frontiers and Challenges*; Hard cover, 374 pages, Publisher: InTech, Published: August 01, 2011

-
- ³⁴Leng J, (Ed); *Shape-Memory Polymers and Multifunctional Composites*, CRC Press, 2010
- ³⁵Hayashi S, Kondo S, Kapadia P & Ushioda E; *Room-Temperature-Functional Shape Memory Polymers*; *Plastics Engineering*; 1995
- ³⁶Liu C, Qin H & Mather P.T.; *Review of progress in shape-memory polymers. Journal of Materials Chemistry*; Vol.17, No.16, 2007 pp. 1543-1558
- ³⁷Lendlein, A., Kelch, S.; *Shape-memory polymers*. *Angew. Chem. Int. Ed.* 41: 2034–2057; 2002
- ³⁸*Id.*
- ³⁹ There is some debate on this issue, but for the purposes of this paper it is assumed that the shape memory effect is not an intrinsic property of all polymers. See generally Marc Behl and Andreas Lendlein; *Shape-memory Polymers*; *Materials Today*, April 2007 Vol 10, No. 4 and compare to Gall, K.; M. Dunn, M.; Liu, Y.; *Internal Stress Storage in Shape Memory Polymer Nanocomposites*; *Appl. Phys. Lett.*, 2004, 85, pp 290
- ⁴⁰Behl M & Lendlein A.; *Shape-memory polymers*; *Materials Today*; Vol.10, No.4, pp. 20-28
- ⁴¹ See Generally: *Id.*; Behl M, Razzaq M.Y., and Lendlein A.; *Multifunctional Shape-Memory Polymers. Advanced Materials*; Vol.22, No.31; 2010; Lendlein A & Kelch S.; *Shape-memory polymers*; *Angewandte Chemie-International Edition*; Vol.41, No.12; 2002; Liu C, Qin H & Mather PT; *Review of progress in shape-memory polymers. Journal of Materials Chemistry*; 2007
- ⁴² *Id.*
- ⁴³Gall, Ken; Yakacki, Christopher M.; Liu, Yiping; Shandas, Robin; Willett, Nick; Anseth, Kristi S.; *Thermomechanics of the shape memory effect in polymers for biomedical applications*; *Journal of Biomedical Materials Research Part A* 2005 Vol: 73(3):339-348.
- ⁴⁴Liu, C.; Qin, H.; Mather, P.T.; *Review of progress in Shape-Memory Polymers. J. Mater. Chem.*, 2007, 17, 1543-1558.
- ⁴⁵ Patrick T. Mather, Xiaofan Luo, and Ingrid A. Rousseau; *Shape Memory Polymer Research: Annual Review of Materials Research*; *Materials Research*; Vol. 39: 445-471 2009.
- ⁴⁶Liu, C.; Qin, H.; Mather, P.T.; *Review of progress in Shape-Memory Polymers. J. Mater. Chem.*, 2007, 17, 1543-1558
- ⁴⁷Kim B.K.; Lee S.Y.; Xu M.; *Polyurethanes having shape memory effects*; *Polymer* 37: 5781, 1996.
- ⁴⁸Liu, C.; Qin, H.; Mather, P.T.; *Review of progress in Shape-Memory Polymers. J. Mater. Chem.*, 2007, 17, 1543-1558

-
- ⁴⁹Gordon, *Proc of First Intl. Conf. Shape Memory and Superelastic Tech.*, 115-120 (1994) and Tobushi et al., *Proc of First Intl. Conf. Shape Memory and Superelastic Tech.*, 109-114 (1994)
- ⁵⁰ European PatentNo..EP0363919 A2, Issued Jan 31, 1996 to Mitsubishi Jukogyo Kabushiki Kaisha
- ⁵¹ All values in brackets denote concentrations
- ⁵² U.S. Patent No. 5,139,832, issued on August 18, 1992 to Shunichi Hayashi, Hiroshi Fujimura, and Makoto Shimizu
- ⁵³U.S. Patent No. 8,299,191, issued on October 30, 2012 to Kenneth Gall, Walter E. Voit, and Taylor Ware
- ⁵⁴U.S. Patent No. 8,101,689, issued on January 24, 2012 to Tat Hung Tong, Benjamin J. Vining, Richard D. Hreha, Thomas J. Barnell
- ⁵⁵*Id.*
- ⁵⁶U.S. Pat. No. 7,276,195, issued on October 2, 2007, to Tat Hung Tong
- ⁵⁷U.S. Pat. No. 6,759,481, issued on July 6, 2004, to Tat Hung Tong
- ⁵⁸Koerner H, Price G, Pearce N, Alexander M, Vaia R.; *Remotely actuated polymer nanocomposites--stress-recovery of carbon-nanotube-filled thermoplastic elastomers*; Nat Mater 2004;3:115; and Mohr R, Kratz K, Weigel T, Lucka-Gabor M, Moneke M, Lendlein A.; *Initiation of shape-memory effect by inductive heating of magnetic nanoparticles in thermoplastic polymers*.ProcNatlAcadSci U S A. 2006 Mar 7;103; Gunes, I.S., Jimenez, G., Jana, S.C.; *Carbonaceous fillers for shape memory actuation of polyurethane composites by resistive heating*; Carbon, 47, 981-997, 2009
- ⁵⁹Lendlein A, Jiang H, Junger O, Langer R.;*Light-induced shape-memory polymers*; Nature 2005;434:879
- ⁶⁰ See for example U.S. Pat. Pub. No. US 2008/0021166 A1, Filing date: Oct 6, 2005; by Tat Tong and Emily Snyder
- ⁶¹Lee, K.M.; Koerner, H.; Vaia, R.A.; Bunning, T.J.; White, T.J.; *Light-activated shape memory of glassy azobenzene liquid crystal polymer network*; Soft Matter 2011, 7, 4318-4324
- ⁶²Huang W, Yang B, An L, Li C, Chan Y.; ApplPhysLett 2005;86:114105.
- ⁶³He Z, Satarkar N, Xie T, Cheng YT, Hilt JZ.; *Remote Controlled Multishape Polymer Nanocomposites with Selective Radiofrequency Actuations*;Adv Mater, Volume 23, Issue 28, pages 3192–3196, July 26, 2011
- ⁶⁴Bellin, I., Kelch, S., Langer, R. &Lendlein, A.;*Polymeric triple-shape materials.*; Proc. Natl. Acad. Sci. U.S.A. 103, 18043-18047 2006
- ⁶⁵Xie T, Xiao X, Cheng Y.; *Revealing Triple-Shape Memory Effect by Polymer Bilayers*; Macromol Rapid Commun; Volume 30, Issue 21, pages 1823–1827, November 2, 2009

-
- ⁶⁶Behl M, Bellin I, Kelch S, Wagermaier W, Lendlein A.; *Magnetic Memory Effect of Nanocomposites*; AdvFunct Mater 2009;19:102.
- ⁶⁷Behl M, Lendlein A.; *Triple-shape Polymers*; J Mater Chem 2010;20:3335.
- ⁶⁸Ahn S, Deshmukh P, Kasi R.; *Shape Memory Behavior of Side-Chain Liquid Crystalline Polymer Networks Triggered by Dual Transition Temperatures*; Macromolecules 2010;43:7330
- ⁶⁹Zotzmann J, Behl M, Feng Y, Lendlein A.; *Copolymer networks based on poly(omega-pentadecalactone) and Poly(epsilon-caprolactone) segments as a versatile triple-shape polymer system*; Adv. Funct. Mater. 20 (20), 3583-3594 2010
- ⁷⁰Chen S, Hu J, Yuen C, Chan L, Zhuo H.; *Triple shape memory effect in multiple crystalline polyurethanes*; PolymAdvTechnol 2010;21:377.
- ⁷¹Xie T, Xiao X, Cheng Y.; *Revealing Triple-Shape Memory Effect by Polymer Bilayers*; Macromol Rapid Commun 2009;30:1823.
- ⁷²Luo X, Mather P.; *Triple-Shape Polymeric Composites*; AdvFunct Mater 2010:2649e56.
- ⁷³Kolesov I, Radusch H; *Multiple shape-memory behavior and thermal-mechanical properties of peroxide cross-linked blends of linear and short-chain branched polyethylenes*; eXPRESS Polymer Letters, 2(7), 461-473 (2008).
- ⁷⁴DiOrio A, Luo X, Lee K, Mather P.; *A Functionally Graded Shape Memory Polymer*; Soft Matter 7 68-74; 2011.
- ⁷⁵Sun L, Huang W.; *Mechanisms of the multi-shape memory effect and temperature memory effect in shape memory polymers*. Soft Matter 20106:(18): 4403-6.