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Shape Memory Polymers

Literature Review

John A. Hiltz

Defence R&D Canada

Technical Memorandum

DRDC Atlantic TM 2002-127

August 2002

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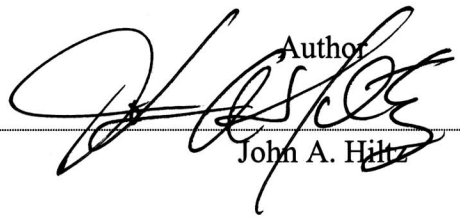


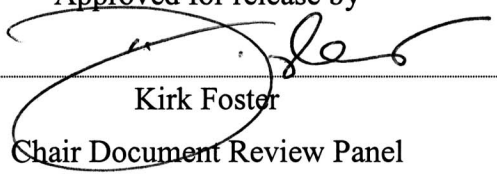
John A. Hiltz

Approved by

Richard Morchat

Section Head Emerging Materials Section

Approved for release by



Kirk Foster

Chair Document Review Panel

Abstract

Shape memory polymers (SMPs) are materials that have properties, such as Young's modulus, that change in response to an external stimulus. As such they are one of a number of materials, including shape memory alloys (SMAs) and ceramics, that can be used as adaptive materials in intelligent systems.

In this memorandum, the literature pertaining to shape memory polymers is reviewed. Topics covered include the history of the development and commercialization of SMPs, the basis of the shape memory effect in polymers, the advantages and disadvantages of SMPs, applications of SMPs, the description of linear and nonlinear constitutive models proposed for SMPs, and the potential to develop poly(urethane) based SMPs with tailored properties.

Résumé

Les polymères à mémoire de forme (SMP) sont des matériaux qui, tel le module de Young, ont des propriétés qui changent par réaction à un stimulus externe. Ils appartiennent donc, à ce titre, à un certain nombre de matériaux dont les alliages à mémoire de forme (SMP) et les céramiques, qu'on peut utiliser comme matériels adaptatifs dans les systèmes intelligents.

Dans le présent mémoire, on revoit la documentation sur les polymères à mémoire de forme. On y traite l'histoire de la création et de la commercialisation des SMP, le fondement de l'effet de la mémoire de forme dans les polymères, les avantages et les inconvénients des SMP, les applications des SMP, la description des modèles constitutifs linéaires et non linéaires proposés pour les SMP et la possibilité de créer à partir de SMP du poly(uréthanne) ayant des propriétés sur mesure.

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Executive summary

Introduction

Shape memory polymers (SMPs) are one of a number of materials, including shape memory alloys (SMAs) and ceramics, which are termed intelligent or adaptive materials. These materials have properties that change in response to an external stimulus. For SMPs the external stimulus is temperature and the property is Young' s modulus.

In this memorandum, the literature pertaining to shape memory polymers is reviewed. Topics covered include the history of the development and commercialization of SMPs, the basis of the shape memory effect in polymers, the advantages and disadvantages of SMPs, applications of SMPs, the description of linear and nonlinear constitutive models proposed for SMPs, and the potential to develop poly(urethane) based SMPs with tailored properties.

Principal results

SMPs are a class of intelligent or adaptive materials that offer great promise in a number of applications. This promise is based on properties that differentiate them from other adaptive materials such as SMAs and ceramics. Compared to SMAs, SMPs are light weight, are capable of hundreds of percent recovery strain, can be processed using standard polymer processing techniques, are low cost, and are electrical and thermal insulators.

The low modulus of SMPs is a drawback in some applications. However, improvements are being sought through the incorporation of reinforcing fibres. The low mass and volume of shape memory foams make them attractive materials for defence and space applications. Parts can be fabricated, their shape modified (in general compacted), and then changed back once in the field or in space.

SMPs are finding application in medical devices such as splints, surgical staples, and intra-arterial catheters. Each of these applications has the potential to improve first line medical care of the soldier in the field.

SMPs, SMPs with fibre reinforced composites, and SMPs fibre reinforced composites have been investigated for active vibration and acoustic control and/or shape control.

The development of poly(urethane) based SMPs with tailored properties and the potential to tailor the properties of SMPs should result in an increase in their applications.

Linear and nonlinear thermomechanical constitutive models have been developed to describe the response of SMPs. These models are useful for the design of SMP elements in which the amount of strain recovery, recovery force, and lower and upper working temperatures are defined.

Significance of Results

The literature review indicates that SMPs are candidate materials for defence applications where mass and volume are critical. The ability to tailor SMP properties will increase their utility in defence applications.

Hiltz, J. A., 2002. Shape Memory Polymers – Literature Review. TM 2002-127. Defence R&D Canada – Atlantic.

Sommaire

Les polymères à mémoire de forme (SMP) font partie d'un certain nombre de matériaux dont les alliages à mémoire de forme et les céramiques, qu'on dit intelligents ou adaptatifs. Ils ont des propriétés qui changent par réaction à un stimulus externe.

Dans le présent mémoire, on revoit la documentation sur les polymères à mémoire de forme. On y traite l'histoire de la création et de la commercialisation des SMP, le fondement de l'effet de la mémoire de forme dans les polymères, les avantages et les inconvénients des SMP, les applications des SMP, la description des modèles constitutifs linéaires et non linéaires proposés pour les SMP et la possibilité de créer à partir de SMP du poly(uréthanne) ayant des propriétés sur mesure.

Résultats principaux

Les SMP sont une classe de matériaux intelligents ou adaptatifs qui promettent beaucoup dans un certain nombre d'applications et ce, grâce à des propriétés qui les différencient des autres matériaux adaptatifs tels que les SMA et les céramiques. En effet, comparés aux SMA et aux céramiques, les SMP sont légers, capables d'un taux de récupération après déformation atteignant plusieurs centaines de pour cent, transformables à l'aide des techniques normales de transformation des polymères, peu coûteux et sont des isolants électriques et thermaux.

Le faible module des SMP constitue un défaut dans certaines applications, mais on est à apporter des améliorations par l'insertion de fibres de renforcement. La faiblesse de la masse et du volume des mousses à mémoire de forme les rend attrayants pour des applications de défense et de techniques spatiales. On peut fabriquer des pièces dont la forme (en général tassée) peut être modifiée et remise à son état original une fois sur le terrain ou dans l'espace.

Les SMP trouvent leur application dans des outils médicaux tels que les gouttières, les agrafes chirurgicales et les cathéters intraartériels. Chacune de ces applications offre la possibilité d'améliorer le soin médical prodigué au soldat sur le terrain.

Les SMP, les SMP contenant des composites aux fibres et les composites de SMP renforcés aux fibres ont été étudiés en vue du contrôle de la vibration et de l'acoustique et/ou de la forme.

La fabrication de poly(uréthanne) à partir de SMP ayant des propriétés sur mesure et la possibilité de personnaliser les priorités des SMP devraient contribuer à l'accroissement des applications des SMP.

Les modèles constitutifs thermomécaniques linéaires et non linéaires ont été créés pour décrire la réaction des SMP. Ces modèles servent à la conception des éléments des SMP dont la récupération de déformation, la force de récupération ainsi que les températures inférieures et supérieures de marche sont définies.

Portée des résultats

L’analyse documentaire indique que les SMP sont des matériaux qui se prêtent aux applications de défense dont la masse et le volume sont essentiels. On les utilisera de plus en plus dans les applications de défense car on peut facilement adapter leurs propriétés.

Hiltz, J. A., 2002. Shape Memory Polymers – Literature Review. TM 2002-127. R & D pour la défense Canada – Atlantique.

Table of contents

List of figures

List of tables

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Introduction

There are materials including metals, ceramics and polymers, that recover mechanically induced strain when heated. These materials are referred to as shape memory materials (1). Monkman (2) notes that although shape memory polymers (SMPs) have similar characteristics to shape memory alloys (SMAs), the relationship stops there, as the basic physical principles are very different. The shape memory effect of a SMA arises from the introduction of a plastic deformation at a temperature that becomes elastic upon heating. This allows the alloy to return to its original shape. In addition, the elastic modulus is normally observed to increase with heating for SMAs. By comparison, SMPs rely on a glass transition or the melting of a crystalline phase to effect a change in state (for instance, Young's modulus). The modulus decreases as the polymer is heated through the glass transition temperature (T_g) or the crystalline melting temperature (T_m).

A comparison of the free recovery strains and constrained recovery forces for ceramic, metal and polymeric shape memory materials are shown in Table 1 (3).

Table 1. Comparison of the unconstrained recovery stress and constrained recovery stress for ceramic, metal and polymeric shape memory materials.

	CERAMICS	METALS	POLYMERS
Unconstrained recovery strain	~1%	~7%	~400%
Constrained recovery stress	~100MPa	~500MPa	~3MPa

From reference 3

It can be seen in Table 1 that the recovery strain is significantly higher and the constrained recovery stress significantly lower for shape memory polymers than for ceramic or metal shape memory materials. A more thorough comparison of Titanium/Nickel shape memory alloys and polymeric shape memory polymer properties is shown in Table 2 (4).

From Table 2 a number of other very significant differences between shape memory alloys and shape memory polymers, in addition to recovery stress and strain, can be seen. These include temperature induced changes, density, processibility, cost and thermal conductivity.

In this memorandum, the literature concerning shape memory polymers is reviewed. The review includes the basis of the shape memory effect, the advantages and disadvantages of SMPs compared to shape memory alloys, the properties of SMPs, the chemistry of SMPs, and modelling of the SMP effect.

Table 2. Comparison of properties of Ti/Ni shape memory alloys and shape memory polymers.

MATERIAL/PROPERTY	TI/NI SHAPE MEMORY ALLOY	SHAPE MEMORY POLYMER
Recovery Stress	200-400 MPa	1-3 MPa
Recovery strain	6%	50-600%
At low temperature	Soft (E_l)	Hard (E_l=100E_h)
At high temperature	Hard (E_h = 2E_l)	Soft (E_h)
Density	6-7 g/cm^3	1 g/cm^3
Phase transformations	Martensitic, R-phase	Glass Transition
Shaping	Difficult	Easy
Cost	Expensive	Cheap
Heat conductivity	High	Low

History

The first shape memory polymer, a poly(norbornene) based polymer, was reported by CdF-Chimie Company, France, in 1984 (5) and was made commercially available in the same year by Nippon Zeon Company of Japan (6) under the trade name Norsorex This polymer has a T_g of between 35°C and 40°C but applications have been limited by its processibility.

The Kurare Corporation, Japan, developed a second commercial SMP, Kurare TP-301, in 1987. It is poly(trans-isoprene) based , has a T_g of -68 °C and a melting temperature (T_m) of 67 °C, but like poly(norbornene) has limited processibility (7).

A third commercial SMP, Asmer, was introduced by Asahi Company, Japan and is poly(styrene-butadiene) based with T_gs in the 60°C to 90°C range (7).

Diisocyanate/polyol based polyurethane SMPs were developed by Mitsubishi Heavy Industries in the late 1980s (8). Poly(urethane) based SMPs are available under a number of trade names including Diary MM-4510, a polyester polyol based poly(urethane) and Diary MM-4520, a polyether polyol based poly(urethane). The advantage of the poly(urethane) SMPs is the flexibility that the polyurethane chemistry provides in designing materials with a range of T_gs and therefore temperatures where the shape memory effect can be invoked. In addition, these poly(urethanes) are thermoplastic polymers which provides a significant improvement in processibility.

Nippon Zeon has produced a series of polyester based SMPs that are marketed under the trade name Shable.

Through the nineties, most of the development and applications of SMPs discussed in the literature concerned thermoplastic poly(urethane) based SMPs. There are a number of reasons for this. The most important is the ability to control the structure and therefore properties of poly(urethanes). In particular, the ability to vary the glass transition temperature of this SMP over a wide temperature range increases the potential applications. The thermoplastic nature of poly(urethanes) renders them amenable to processing by techniques such as extrusion, injection or blow molding or by solution casting. Poly(urethanes) also have good chemical and ultraviolet resistance and biocompatibility compared to other SMPs (9).

In 1997, Liang et. al. (6) proposed the use of shape memory composites to address the low strength and stiffness of SMPs. They investigated the preparation of poly(urethane) SMPs composites using chopped glass, unidirectional Kevlar™, and woven fibreglass. More recently, the properties of SMP composites fabricated using resin transfer molding and pre-impregnation of fibre tows (Elastic Memory Composite™) have been reported (1). The matrix resin was an epoxy based thermoset resin that, by contolling the degree of cross-linking, can have T_gs ranging from –13°C to 95 °C.

The Shape Memory Effect

The basis of the shape memory effect in polymeric materials is a large difference in Young's modulus (E) of a material below and above a 'phase' transition temperature. For thermoplastic poly(urethane) based SMPs the large change in E takes place at the T_g. For other SMPs, such as those based on trans-poly(isoprene), the change in E takes place at the melting point (T_m) of the crystalline phase of the polymer. For both polymers the modulus changes significantly at the phase transition temperature, decreasing as the polymer is heated from below the transition temperature to above the transition temperature. As a result of this, strain can be introduced into the polymer with relative ease at temperatures above the transition temperature. If the strain is maintained and the temperature of the material is decreased below the transition temperature, the strain is 'frozen in'. This strain is recovered when the polymer is heated above the transition temperature again.

At the molecular level the 'frozen in' strain is explained as resulting from the lack of micro-Brownian motion of the polymer chains at the lower temperatures, that is, at temperatures below the glass transition temperature or the crystalline melting temperature (10-12). Micro-Brownian motion of the 'soft' segments at temperatures above the transition temperature leads to relaxation of an applied strain if the polymer is unloaded at this temperature. This relaxation process is severely retarded when the polymer is cooled below the transition temperature while maintaining the applied load and the 'shape' induced by the high temperature loading is fixed.

A thermomechanical cycle of a shape memory polymer is shown in Figure 1. The cycle consists of four stages, marked as 1 through 4 in Figure 1. In stage 1, a stress (σ_m) is applied at a temperature (T_h) above the transition temperature and results in a maximum strain (ε_m). In stage 2, the strain is maintained and the polymer is cooled to a temperature (T_l) below the transition temperature and held at that temperature for a period of time. During the cooling process the stress increases to σ_l. In stage 3, the sample is unloaded and the strain assumes a value for the unloaded condition (ε_u). In stage 4 the sample is heated to T_h. Most of the strain introduced in the first step of the cycle is recovered. However, some residual strain (ε_p) remains.

Thermomechanical testing is often continued for a number of cycles to determine the effect of the number of cycles on the ε_m, ε_u, and ε_p. The relationships between strains ε_m, ε_u, and ε_p are used to evaluate the shape fixity (R_f) and strain recovery (R_r) of the SMP.

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} X 100\% \qquad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_p(n)}{\varepsilon_m - \varepsilon_p(n-1)} X 100\% \qquad (2)$$

n and n-1 refer to the n^{th} and n^{th} –1 cycles for cyclic testing using the above stress, strain, temperature cycle.

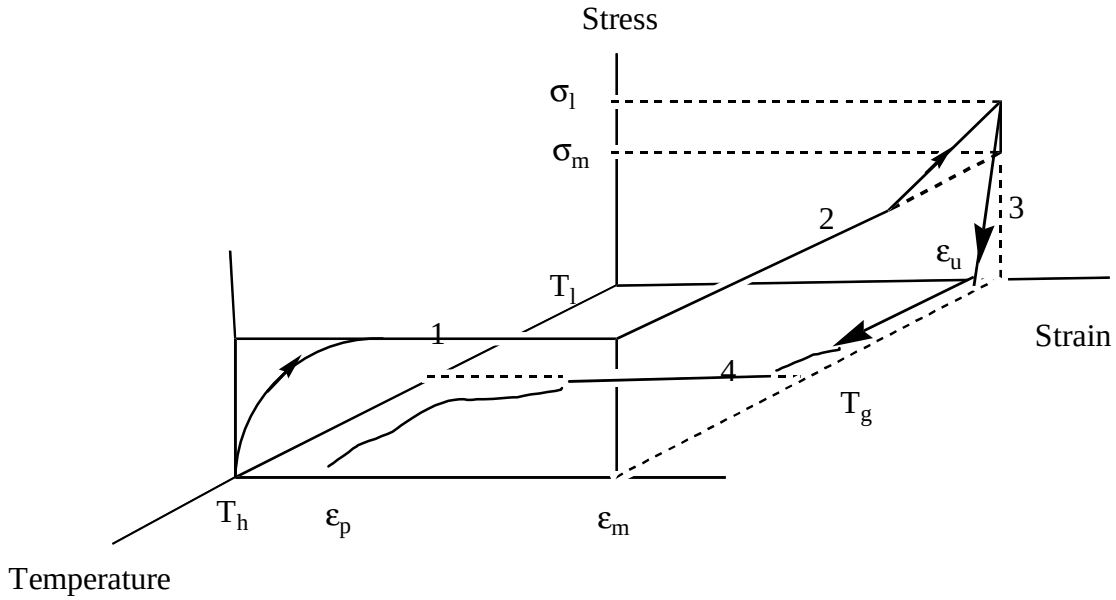

Figure 1. Thermomechanical cycle for a shape memory polymer.

Tobushi et. al. (10,11,13) have investigated the effect of cyclic and thermomechanical testing on the stress-strain response, shape fixity, shape recoverability, creep recovery of poly(ester)urethane SMPs. They found that stress and strain curves varied significantly following cyclic deformation above T_g for low numbers of cycles but the variation decreased as the number of cycles increased. Shape fixity and shape recovery were not found to vary significantly when the sample was subjected to the temperature/stress strain (thermomechanical) cycle shown in Figure 1. For instance, R_f varied between 98% and 99% percent for maximum strains of 20%, 50%, 100% and 200% and 10 thermomechanical cycles. R_r was approximately 90% to 95% for one mechanical cycle and maximum strains of 20%, 50%, 100% and 200% and approached 100% for more than 4 thermomechanical cycles. Creep strain was recovered for samples loaded and unloaded above T_g, but was not recovered for samples loaded and unloaded below T_g.

The shape fixity and shape recovery of thin films of poly(ester)urethane SMPs were also investigated following loading at various temperatures. Two SMPs, with T_gs of ~25°C and ~55°C, were investigated. Shape fixity was found to be 98% for loading at temperatures above T_g, but decreased with increasing thermomechanical cycles for loading at temperatures below T_g. Strain recovery for loading above T_g was 98% except for the first few cycles. The testing indicated that thermomechanical response of the two materials were similar.

Advantages/Disadvantages of Shape Memory Polymers Compared to Shape Memory Alloys

The comparison of properties of SMPs and shape memory alloys (SMAs) in Table 2 indicate the majority of advantages and disadvantages of these classes of shape memory materials.

Polymers are less dense than metallic alloys and therefore offer a weight advantage per unit volume of material.

The constrained force that can be generated from SMPs is a fraction of the constrained force that can be generated by SMAs, while the recovery strains are orders of magnitude higher.

The change in elastic modulus of SMPs is reversible without hysteresis in the vicinity of the T_g (6). That is, there is a monotonic relationship between temperature and elastic modulus. This is not observed for SMAs.

SMPs exhibit ease of processibility (formability and workability) and are lower in cost than SMAs (7, 14,15).

The thermal conductivity of SMPs is much lower than the thermal conductivity of SMAs. This can be seen as an advantage or a disadvantage. Low thermal conductivity is desirable if the thermal insulation is required. It is a disadvantage if an SMP is used in an application where heat flow into or out of the polymer in a short period of time is desirable (16). One approach to overcoming the low thermal conductivity of SMPs is to use SMP foams (2). The high permeability of foams allows them to be heated and cooled quickly compared to solid polymeric materials.

Applications of SMPs

One of the most common applications of the shape memory effect is in heat shrink tubing. The tubing is deformed (stretched) at high temperature, cooled while the deformation is maintained, and after heating returns to its prestretched shape (shrinks).

In 1997 it was noted that applications of SMPs were limited (6). However, the literature indicates that applications/potential applications of intelligent or adaptive polymeric materials, such as SMPs, abound. Applications include use in clothing materials, in medical devices, for damping and active vibration control, for pipe joining, for sealing, and for load bearing and non-load bearing structural materials. Polymers with shape memory capability have other properties, such as moisture permeability, specific volume, refractive index and loss factor, that change significantly at the glass transition temperature. As such these materials can be referred to as intelligent or adaptive materials, one aspect of which is the shape memory effect. Some of the applications reviewed in the following paragraphs depend not only on the shape memory effect, but also on material properties changes in the glass transition region.

Clothing Materials

The water vapour permeability of polymers with shape memory capability changes in the vicinity of the glass or melting point transitions (4, 14, 17-19). This property has been used to design 'breathable' clothing, including rainwear, inner soles and boot coverings. For instance, polyurethane coatings that impart water resistance have been incorporated into rainwear. The water vapour permeability of these coatings increases substantially as they are heated through the phase transition temperature. This imparts increased breathability at higher temperatures and improves the comfort associated with wearing these garments.

Medical

SMPs have been proposed for a number of medical applications including catheters, bone casts, stents, and endotrachial devices (20), surgical staples (21), intra-arterial catheters, orthopaedic braces and splints, and contact lens (22).

Poly(urethane) based SMPs have good biocompatibility and anti-thrombus properties. These properties make them candidates for applications such as catheters, artificial blood vessels, muscle, and contact lens. The SMP would be designed to have a Tg below body temperature. For an intra-arterial catheter application, the SMP would be inserted into the patient in the glassy state. In the body the catheter would be warmed above the T_g and soften, minimizing the chance of damaging the arterial wall. A contact lens would be designed in the same way. That is, it would be in glassy state at room temperature allowing ease of handling but have a T_g less than body temperature and therefore soften once placed onto the eye.

The use of SMP for surgical staples has been investigated. The proposed material has a T_g of 37^oC, and a modulus of ~750 MPa at 24^oC and ~430 MPa at 37^oC. The staple material is formed in the closed (permanent) shape, then heated above its transition temperature and

formed into the temporary (open) shape and cooled. When placed in the body it is heated and reverts to its permanent (closed) shape.

SMPs are also being investigated for use in fracture fixation (23). The fracture fixation device is flat as received. It is heated and shaped to the patient, and then cooled to fix its shape. The original flat shape can be recovered by heating the device above the T_g.

Damping

SMPs have been investigated for use as constrained layer damping materials in fibre reinforced composites (24). By controlling the temperature of the SMP in the fibre reinforced composite, the damping resulting from the incorporated SMP can be varied. In the system investigated, a poly(urethane) based SMP ($T_g \sim 45\,^{o}C$) was incorporated into a glass/carbon fibre composite. The carbon fibre was used to heat the SMP and alter/control the damping characteristics of the composite.

Composites of SMPs with high performance reinforcing fibres have the potential to be used as adaptive structural materials for active vibration and acoustic control and/or active shape control (6). SMP composites have higher in plane strength and modulus while maintaining shape and elastic memory properties of the polymeric component.

The temperature dependent acoustic properties of SMPs vary in the vicinity of T_g (2). Tests carried out on SMP polymer foams in a number of thicknesses revealed a shift in resonance of several hundred Hertz (Hz) at a nominal frequency of 2.5 kHz. This indicates SMP polymer foam resonance frequencies can be 'tuned' by changing temperature.

Structural Materials

The feasibility of using SMPs in open cellular (foam) form as low mass, low volume, and low-cost self deployable structures for space and commercial applications has been confirmed (16). The concept has been termed 'cold hibernated elastic memory' or CHEM. A number of advantages for CHEM based structures have been delineated and include low mass, low storage volume, high reliability (no deployment mechanisms are required), high dynamic damping, ease of fabrication, impact and radiation resistance, and thermal and electrical insulation. An obvious drawback is that deployment requires a source of heat to deploy the structure. Potential applications include support structures for telecommunications subsystems such as struts and beams, as wheels, chassis, and masts for rover subsystems, as low frequency parabolic antennas, in radar structures, as a solar array deployment device, as for space habitats including shelters and hangars.

A subsequent investigation of the effect of cold hibernation of a CHEM foam indicated that it expanded back to its original shape in approximately 4 days (25). This was attributed to the storage temperature of the foam being to close to the T_g to eliminate all micro-Brownian motion and concomitant relaxation of the applied strain. This points out the importance of selecting SMP materials with transition temperatures that ensure they will perform as expected in the temperature range for the application.

Liang et.al. (6) proposed the use of reinforcing fibres to improve the strength and stiffness of SMPs and allow their use as load bearing structural materials. More recently, carbon reinforced shape memory polymer composites have been investigated (1). These composites, candidate materials for deployable space structures, have a thermoset epoxy based matrix. They have been investigated because of US Department of Defence and NASA interest in truss elements that can be compacted on earth, stored and subsequently transported into space, and then deployed as a rigid structure. To prepare samples, the composite was heated above the T_g of the matrix resin, deformed, and cooled while maintaining the deformation to fix the deformed shape. The study investigated the effect of shape fixation on damage to satin weave and plain weave carbon fibre composites. Preliminary testing indicated that a plain weave fibre and a resin system with a higher strain to failure was less susceptible to fibre buckling. The composites exhibited good recoverability of shape upon heating above the T_g of the resin. The effect of bending (compaction) on the mechanical properties of these composites requires further investigation.

An inflatable truss frame for space applications, fabricated using SMP as the matrix and carbon fibre reinforcement, has also been evaluated (26). The test results showed performance as good as or better than the current-state-of-the-art truss frame.

Other Applications

SMPs have been investigated for use in the active disassembly of electronic products (27-30). This is part of an effort to reduce the cost associated with the end-of-life recycling of electronic. In one application poly(urethane) SMP fasteners were designed and evaluated for the active disassembly of mobile phones. The fasteners were successfully activated, when heated above their T_g, through a reduction of elastic modulus.

Defence Applications

From a defence perspective, there are a number of potential applications for SMPs. Shape memory foams can be used to fabricate parts that are light weight and compact thus easily transported. Once in the 'field', an increase in temperature can be used to regenerate the original shape of the part. These aspects of SMPs, low mass and volume, also make them attractive materials for space applications. Parts can be fabricated, their shape modified (in general compacted), and then changed back once in space. Thermoplastic and thermoset SMPs fibre composites have been investigated for space applications.

As mentioned earlier, SMPs have also been investigated for medical applications such as splints, surgical staples, and intra-arterial catheters. Each of these applications has the potential to improve first line medical care of the soldier in the field.

SMPs and SMP fibre composites have been investigated for vibration and acoustic control and/or shape control. These materials would reduce noise generated by defence platforms. For instance, noise abatement on ships would not only decrease probability of detection but also improve working conditions for ships staff.

Thermomechanical Constitutive Models(31-33)

Linear Thermomechanical Constitutive Model

The three element standard linear viscoelastic (SLV) model consists of a spring and a Maxwell element arranged in parallel. The Maxwell element is composed of a spring and a dashpot arranged in series. The relationship between stress (σ), strain (ε), elastic modulus (E), viscosity (μ) and retardation time (λ) for the SLV model is given by equation 3, where the dot over the quantity indicates the derivative with respect to time. The basic time dependent deformation of viscoelastic materials is well described by this model.

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\mu} - \frac{\varepsilon}{\lambda} \qquad (3)$$

However, the SLV model cannot describe the large changes in the mechanical properties of SMPs in the vicinity of the T_g and differences in creep recovery behaviour above and below T_g.

Tobushi et. al. (31, 32) proposed a four element thermomechanical constitutive model to address the shortcomings of the SLV model. A slip mechanism due to internal friction in the polymer is introduced to address the difference in creep recovery above and below T_g. Coefficients in the model are expressed as single exponential function of temperature to describe the variation in mechanical properties in the vicinity of T_g. The model also takes into account thermal expansion.

The four element model incorporating the slip element is shown in Figure 2. The relationship between stress, strain, viscosity and retardation time is given by equation 4 where ε_s is the irrecoverable creep strain. In this context irrecoverable creep strain refers to creep strain that cannot be recovered at that particular temperature. It does not mean that the creep strain cannot be recovered at another temperature. In fact, this irrecoverable creep strain is the basis for the shape memory effect (34).

The relationship between creep strain (ε_c) and ε_s is given by equation 5. S represents the fraction of creep strain (ε_c) not recovered. The value of S is temperature dependent.

The irrecoverable strain occurs due to slip. Slip may arise from molecular chain orientation or decoupling of cross-links. To produce slip, a force must overcome the internal friction of the polymer. The internal friction of a polymer varies considerably above and below the glass transition temperature. At temperatures above T_g, the internal friction of the polymer is low, but the critical strain value required to produce slip is large. The value of S is small. At temperatures below T_g, the internal friction of the polymer increases substantially. The stress required to overcome this is large but the critical value of the strain to produce slip is substantially lower than at high temperatures. The value of S is large.

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\mu} - \frac{\varepsilon - \varepsilon_s}{\lambda} \qquad (4)$$

$$\varepsilon_s = S(\varepsilon_c) \qquad (5)$$

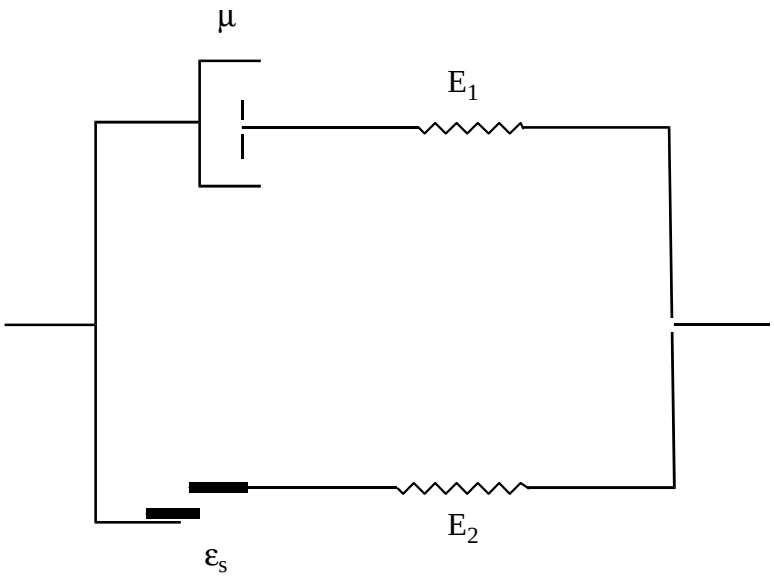

Figure 2. *Four element model proposed by Tobushi et. al. E_1 and E_2 are spring elements, μ is a dashpot and ε_σ is an internal friction element.*

The effect of thermal expansion is assumed to be independent of the stress strain behaviour described by equation 4. The stress-strain-temperature relationship is given by equation 6 where T is temperature and α is the coefficient of thermal expansion.

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\mu} - \frac{\varepsilon - \varepsilon_s}{\lambda} + \alpha\dot{T} \qquad (6)$$

The properties of SMPs vary significantly in the region of the glass transition. A plot of the logarithm of elastic modulus against reciprocal temperature normalized to the glass transition temperature (T_g/T) is shown in Figure 3. In the area of glass transition the relationship between log E and T_g/T is linear and can be described by equation 7 where E_g is the value of the modulus at the glass transition temperature and a_E is the slope of the straight line. T_w is one half of the temperature range of the glass transition. E assumes the value E_h at $T_g + T_w$, and E_l at $T_g + T_w$.

$$\log E - \log E_g = a_E\left(\frac{T_g}{T} - 1\right) \qquad (7)$$

Solving for E, the temperature dependence of the elastic modulus in the glass transition is given by equation 8.

$$E = E_g \exp\{a_E(\frac{T_g}{T} - 1)\} \qquad (8)$$

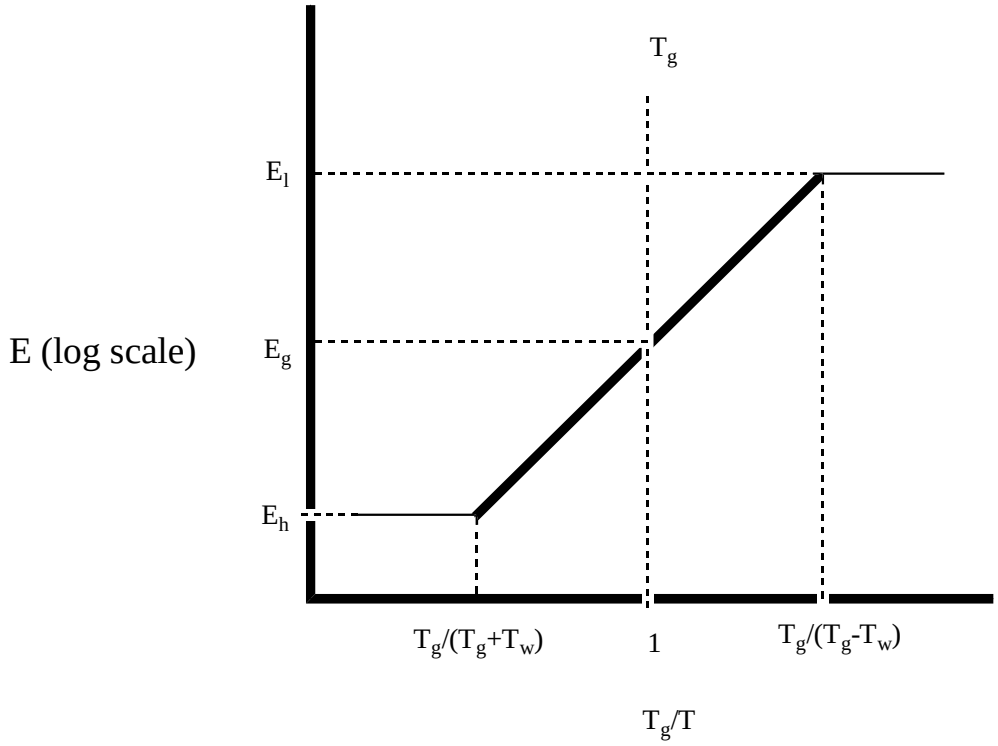

Figure 3. *Plot of logE versus reciprocal temperature normalized to T_g.*

The magnitudes of μ, λ, and S also vary with temperature in the glass transition region. It was assumed that these parameters could be expressed as an exponential function of T in a manner similar to the elastic modulus. These relationships are shown in equations 9-11. These parameters assume constant values at temperatures below and above the glass transition region. For instance, in Figure 3 the value of the elastic modulus is E_l at temperatures below the glass transition range and E_h at temperatures above the glass transition range.

$$\mu = \mu_g \exp\{a_\mu(\frac{T_g}{T} - 1)\} \qquad (9)$$

$$\lambda = \lambda_g \exp\{a_\lambda(\frac{T_g}{T} - 1)\} \qquad (10)$$

$$S = S_g \exp\{a_s(\frac{T_g}{T} - 1)\} \qquad (11)$$

Nonlinear Thermomechanical Constitutive Model

SMPs are capable of recoverable strains of several hundred percent. Even though in most applications they are used at strains below 20%, non-linear strain is observed for strains above 3%. Tobushi et. al. (33) developed a non-linear thermomechanical constitutive model by modifying the linear four element thermomechanical model described in the previous section. The non-linear constitutive equation is shown in equation 12.

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + m(\frac{\sigma - \sigma_y}{k})^{m-1}\frac{\dot{\sigma}}{k} + \frac{\sigma}{\mu} + \frac{1}{b}(\frac{\sigma}{\sigma_c} - 1)^n - \frac{\varepsilon - \varepsilon_s}{\lambda} + \alpha\dot{T} \qquad (12)$$

The modified equation incorporates a power function of stress, $m(\frac{\sigma - \sigma_y}{k})^{m-1}$, to account for non-linear time-independent strain with respect to the linear elastic term , $\frac{\dot{\sigma}}{E}$, and adds a non-linear term, $\frac{1}{b}(\frac{\sigma}{\sigma_c} - 1)^n$, expressed as a power function, to the linear viscous term, $\frac{\sigma}{\mu}$. The terms σ_y and σ_c denote the proportional limits of stress in the time independent term and viscous term respectively. They correspond to the yield stress and creep limit for a material.

The temperature dependence of the parameters, such as E, μ, and λ is expressed in the same manner as for the linear model.

The relationship between irrecoverable strain and creep strain was modified to take into consideration time independent plastic strain (ε_p) resulting from large strains induced by constant strain rate loading. The irrecoverable strain is defined by equation 13.

$$\varepsilon_s = S(\varepsilon_c + \varepsilon_p) \qquad (13)$$

Tailored Poly(urethane) Based SMPs

In the History Section of this Memorandum, several advantages of poly(urethane) based thermoplastic SMPs were listed. These included the ability to tailor the T_g (and therefore the shape memory properties) of poly(urethane)s by changing the components and/or relative proportions of the components used to prepare them. A large ratio of the glassy modulus to the rubbery modulus and the sharpness of the glass transition are other properties that are desirable for SMPs. The reversible change in the glassy and rubbery modulus of poly(urethane)s SMPs can be as high as 500 times (2). A narrow glass transition range results in a rapid recovery of the shape of the polymer.

Shirai and Hayashi (8) have investigated the effect of changing the chemistry of diisocyanate/polyol/diol based poly(urethane)s on the position of the glass transition. The T_g was found to increase for constant isocyanate/OH ratio as the number of benzene rings in the diisocyanate increased. For example, poly(urethane)s made with hexamethylene diisocyanate had lower T_gs than those made from toluene diisocyanate which in turn had lower T_gs than those made from diphenylmethane diisocyanate for constant isocyanate/OH ratios. The molecular weights of the polyol and chain extender (diol) were also found to affect the T_g. For both poly(tetramethylene ether glycol) and poly(propylene glycol), the T_g of the resulting poly(urethane) decreased as the molecular weight of the polyol increased. The T_g increased as the molar ratio of chain extender to diisocyanate increased.

The sharpness of the T_g is dependent on the degree of phase mixing in phase separated poly(urethane)s. An increase in phase mixing results in broadening of the glass transition. Through careful selection of diols and polyols phase mixing can be minimized and the glass transition range narrowed.

Conclusion

SMPs are a class of intelligent or adaptive materials that offer great promise in a number of applications. This promise is based on properties that differentiate them from other adaptive materials such as SMAs and ceramics. Compared to SMAs, SMPs they are light weight, are capable of hundreds of percent recovery strain, can be processed using standard polymer processing techniques, are low cost, and are electrical and thermal insulators.

The low modulus of SMPs is a drawback in some applications. However, improvements are being sought through the incorporation of reinforcing fibres. The low mass and volume of shape memory foams make them attractive materials for defence and space applications. Parts can be fabricated, their shape modified (in general compacted), and then changed back once in the field or in space.

SMPs are finding application in medical devices such as splints, surgical staples, and intra-arterial catheters. Each of these applications has the potential to improve first line medical care of the soldier in the field.

SMPs and SMP fibre reinforced composites have been investigated for vibration and acoustic control and/or shape control.

The development of poly(urethane) based SMPs with tailored properties and the potential to tailor the properties of SMPs should result in an increase in their applications.

Linear and nonlinear thermomechanical constitutive models have been developed to describe the response of SMPs. These models are useful for the design of SMP elements in which the amount of strain recovery, recovery force, and lower and upper working temperatures are defined.

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List of symbols/abbreviations/acronyms/initialisms

DND	Department of National Defence
SMP	Shape memory polymer
SMA	Shape memory alloy
T_g	glass transition temperature
T_m	melting temperature
T_h	temperature above glass transition or melting temperature
T_l	temperature below glass transition or melting temperature
E, E_h, E_l	Young's modulus, Young's modulus at temperature above glass transition region, Young's modulus at temperature below glass transition region
ε, ε_m, ε_u, ε_p	Strain, maximum strain, unloaded strain, permanent strain
σ, σ_m, σ_l, σ_y, σ_c	Stress, maximum stress, stress at low temperature, yield stress, creep limit stress
μ	viscosity
λ	Retardation time
S	Fraction of creep strain not recovered in thermomechanical cycle
X_g	Value of a parameter (X) at the glass transition temperature
a_E	Slope of plot of $\log(E/E_g)$ versus T/T_g

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Shape memory polymers (SMPs) are materials that have properties, such as Young's modulus, that change in response to an external stimulus. As such they are one of a number of materials, including shape memory alloys (SMAs) and ceramics, that can be used as adaptive materials in intelligent systems.

In this memorandum, the literature pertaining to shape memory polymers is reviewed. Topics covered include the history of the development and commercialization of SMPs, the basis of the shape memory effect in polymers, the advantages and disadvantages of SMPs, applications of SMPs, the description of linear and nonlinear constitutive models proposed for SMPs, and the potential to develop poly(urethane) based SMPs with tailored properties.

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