Part II

Shape memory materials

6

Introduction to shape memory materials

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6.1 Overview

Shape memory materials (SMMs) are a set of materials that, due to external stimulus, can change their shape from some temporary deformed shape to a previously 'programmed' shape. The shape change is activated most often by changing the surrounding temperature, but with certain materials also stress, magnetic field, electric field, pH-value, UV light and even water can be the triggering stimulus [1–5]. When sensing this material specific stimulus, SMMs can exhibit dramatic deformations in a stress free recovery. On the other hand, if the SMM is prevented from recovering this initial strain, a recovery stress (tensile stress) is induced, and the SMM actuator can perform work. This situation where SMA deforms under load is called restrained recovery [6].

Because of the wide variety of different activation stimuli and the ability to exhibit actuation or some other pre-determined response, SMMs can be utilised to control or tune many technical parameters in smart material systems in response to environmental changes – such as shape, position, strain, stiffness, natural frequency, damping, friction and water vapour penetration [1, 2]. Today, a large variety of alloys, ceramics, polymers and gels have been found to exhibit shape memory behaviour. Both the fundamental theories and engineering aspects of SMMs have been investigated extensively and a rather wide variety of different SMMs are presently commercial materials.

Commercialised shape memory products have been based mainly on metallic shape memory alloys (SMAs), either taking advantage of the shape change due the *shape memory effect* or the *superelasticty* of the material, the two main phenomena of SMAs. Shape memory polymers (SMPs) and shape memory gels are developed at a quick rate, and within the last few years also some products based on magnetic shape memory alloys have been commercialised. Shape memory ceramic (SMC) materials, which can be activated not only by temperature but also by elastic energy, electric or magnetic field, are mainly at the research stage.

Although the largest commercial successes have no doubt been seen in the fields of bioengineering and biomedical applications, shape memory materials are becoming increasingly important in many other technological fields including high-performance aircraft and automotive components, space applications, vibration and seismic applications, micro-electromechanical systems (MEMS), telecommunications, polymer matrix composites and many others, including textiles and the clothing sector.

6.2 Shape memory alloys

6.2.1 History

The first milestone in the history of shape memory materials was the discovery of the pseudoelastic behaviour of the Au-Cd alloy in 1932 by Swedish physicist Arne Olander [7]. Later in 1938 Greninger and Mooradian observed the formation and disappearance of a martensitic phase by decreasing and increasing the temperature of a Cu-Zn alloy. In 1949 Kurdjumov and Khandros reported more widely the phenomenon of the memory effect and the thermoelastic behaviour of the martensite phase, soon followed by Chang and Read in 1951 [8].

However, it was not until the early 1960s that the 'revolution' of shape memory materials really began. William J. Buehler and his co-workers at the US Naval Ordnance Laboratory accidentally discovered the shape memory effect in an equiatomic nickel-titanium (NiTi) alloy [9]. Later this alloy was commercialised under the trade name Nitinol (an acronym for NIckel TItanium Naval Ordnance Laboratories). Since the birth of Nitinol, extremely intensive research has been done worldwide to clarify the characteristics of the basic behaviour of the shape memory effect. Today NiTi alloys are the most studied and best characterised of all the alloys ever found with shape memory behaviour.

6.2.2 General principles of shape memory alloys

Shape-memory alloys are metal compounds, which can memorise a predetermined shape, and after being bent, stretched or otherwise mechanically deformed they can return to this shape under certain temperature conditions. This shape-memory effect is due to a phenomenon known as a *thermoelastic martensitic transformation*, which is a reversible, diffusionless transformation between two different crystal microstructures that occurs when a shape-memory alloy is heated or cooled beyond alloy specific *transition temperatures*. These temperature dependent crystal structures or phases are called *martensite* (low temperature) and *austenite* (high temperature) [9].

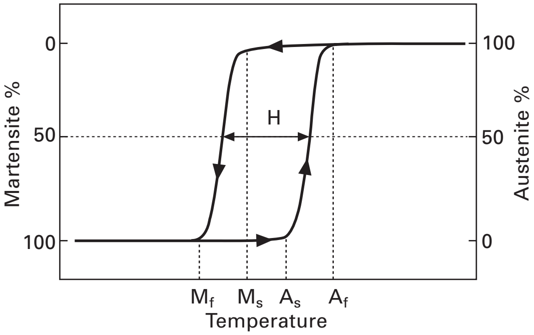
Shape memory alloy is quite strong and hard in its austenite (parent) form, but in the martensite form it is soft and ductile and can easily be deformed. SMAs also exhibit *superelasticy* (or *pseudoelasticity*) giving the material a rubber-like behaviour. The application specific overall austenitic shape (*parent shape)* of SMA is formed and locked (programmed) through a specific high-temperature tempering process.

During the early years of SMAs, a wide variety of alloys have been developed to exhibit the shape memory effect, but only those that can recover substantial amounts of strain or that generate significant force when changing shape are of commercial interest. Today, alloys fulfilling this criterion are mainly the nickel-titanium alloys (NiTi) and copper-base alloys such as CuZnAl and CuAlNi. The characteristics of SMAs that are given in the following pages are mainly based on NiTi alloys.

Hysteresis

When martensite NiTi is heated, it begins to change into austenite (Fig. 6.1). The temperature at which this phenomenon starts is called austenite start temperature (A_s). The temperature at which this phenomenon is complete is called austenite finish temperature (A_f). When austenite NiTi is cooled, it begins to change into martensite. The temperature at which this phenomenon starts is called martensite start temperature (M_s). The temperature at which martensite is again completely reverted is called martensite finish temperature (M_f) [9].

The temperature at which the martensite-to-austenite transformation takes place upon heating is somewhat higher than that for the reverse transformation when cooling. The difference between the transition temperatures when heating and cooling is called hysteresis. Hysteresis is generally defined as the difference between the temperatures at which the material is 50% transformed to austenite upon heating and 50% transformed to martensite upon cooling (see Fig. 6.1). This difference can be up to 20–30 °C [9]. When thinking of medical



6.1 Martensitic transformation and hysteresis (= H) upon a change of temperature.

applications, this practically means that an alloy designed to be completely transformed by body temperature upon heating (Af < 37 °C) would require cooling to about +5 °C to fully retransform into martensite (M_f) [8].

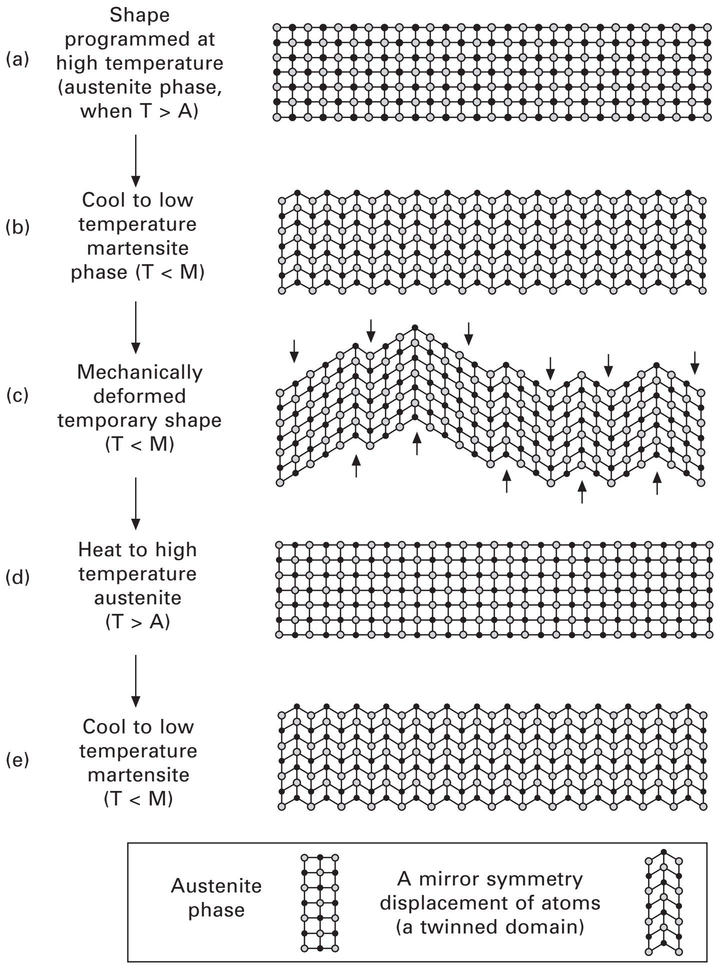
Thermoelastic martensitic transformation

The unique behaviour of NiTi is based on the austenite-to-martensite phase transformations on an atomic scale. The SMA behaviour during the martensitic transformations is very complicated and still not completely understood. The austenite-to-martensite phase transformation can be either temperature induced, known as *thermoelastic martensitic transformation,* or between certain temperature limits also stress induced transformation (pseudoelasticity or superelasticity).

The phenomena causing the shape recovery in thermoelastic transformation is a result of the need of the crystal lattice structure to accommodate to the minimum energy state for a given temperature [7]. If we could look into a NiTi alloy in the atomic scale we could see nickel and titanium atoms arranged alternately in a crystal lattice structure. In the austenite high-temperature form the lattice structure is a simple cubic structure (Fig. 6.2(a)) having a strong symmetry, which prevents it from shifting or changing orientation to accommodate an applied stress. This is the reason why austenitic alloys are much more rigid than martensitic ones.

When a high-temperature austenite is cooled to M_s, the austenite-to-martensite phase transformation begins. This is a diffusionless transformation in which the atoms move only short distances in order to join the new phase (on the order of the interatomic spacing). When the alloy is cooled below M_f, it is entirely in its martensitic phase being now soft and malleable, just waiting to become mechanically deformed out of its original programmed shape to a new 'temporary shape'. During the cooling process the overall macroscopic shape of the alloy does not change significantly. However, in order to maintain the overall shape during cooling and to accommodate to the minimum energy state, the alloy deforms (self-accommodates) the structure of its crystal lattice to a diamond shape structure (Fig. 6.2(b)). The mechanism by which single martensite variants deform is called *twinning*, and it can be described as a mirror symmetry displacement of atoms across a particular atom plane, the twinning plane [9, 10].

Now, if we mechanically deform the soft martensite to a desired temporary shape, the alloy system minimises its energy by continuing twin boundary movement (Fig. 6.2(c) and 6.2(d)). When most metals deform by slip or dislocation, NiTi responds to stress by simply changing the orientation of its crystal structure through the movement of twin boundaries. Next, whenever this deformed martensite is heated above the temperature A_s, the martensite-



6.2 Schematic illustrations of the phase transitions and crystal lattice structures during the shape-memory effect.

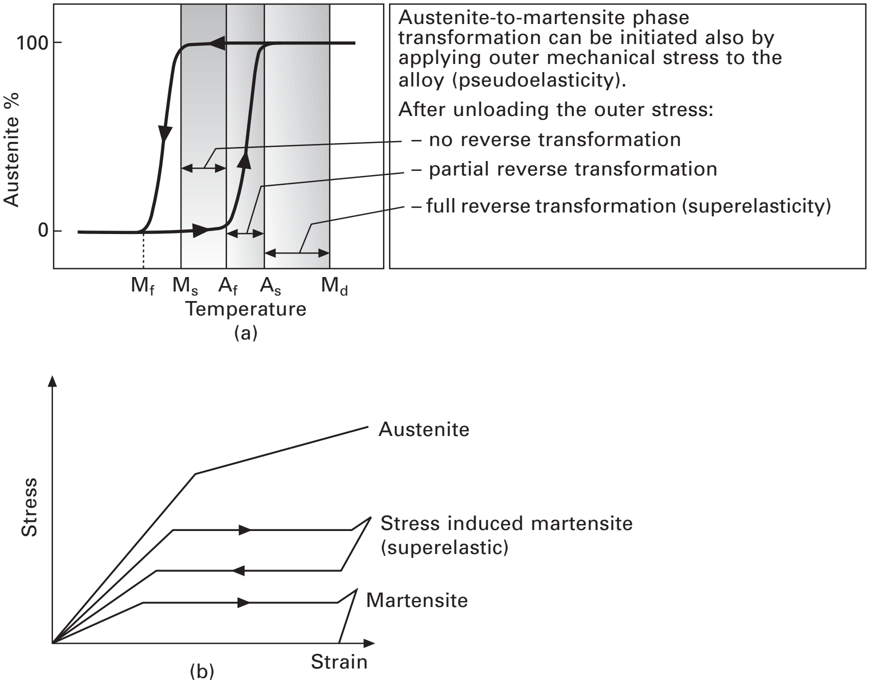
to-austenite phase change starts and the alloy returns to its original programmed austenite crystal structure and to the original macroscopic and rigid shape (Fig. 6.2(e)).

Shape memory effect

The above described macroscale phenomenon, where materials exhibit shape memory upon heating, is called a *one-way shape memory effect* (SME). When the shape change follows a process of free recovery, no reverse shape change in subsequent recooling normally occurs, so the specimen needs to be strained again to repeat the SME. However, a *two-way shape memory* *effect*, where the alloy remembers its low-temperature and high-temperature configurations, can be imparted to an SMA with appropriate training. Special alternative training processes can be used to build up two-way SME, first a specific heat treatment, and then several complicated and time-consuming thermomechanical cycles. Two-way SMAs have much lower recoverable strain and the low-temperature recovery forces are very small compared to the values in the one-way shape memory effect [11].

Superelasticity

Another important phenomenon affecting the shape change of SMA is *Superelasticity*. As can be seen from Fig. 6.3(a), an austenite SMA normally stays in austenite form when the temperature is above M_s. However, when the temperature is only slightly above M_s, a martensitic phase transformation from austenite-to-martensite can be initiated by applying outer mechanical stress to the alloy. An increase in the applied stress produces an effect analogous to a decrease in temperature. However, only one martensite variant (stress



6.3 Austenite-to-martensite phase transformation due to outer mechanical stress: (a) temperature ranges for stress-induced phase transformations; (b) stress-strain behaviour of different phases of SMA at constant temperature.

induced martensite, SIM) grows in the direction most favourable for the applied stress. When the temperature is in the range of $M_s < T < A_s$, SIM will be formed, but after unloading the material will remain as martensite. Partial reversion to austenite will take place upon stress release when temperature is in the range of $A_s < T < A_f$. The complete reverse transformation takes place immediately upon stress release at temperatures approaching or greater than A_f. This full reverse transformation upon stress release is called superelasticity. The alloy provides the same force of the deformation stress and has a rubber-like property (Fig. 6.3b). Superelasticity can be observed only over a specific temperature area. The highest temperature where martensite can be stress induced is called M_d. Above this temperature the austenite alloy can be deformed like ordinary materials by slipping [6, 8, 12].

Mechanical properties of shape memory alloys

Since the birth of NiTi several other alloy types have been discovered. Yet only two main types of SMAs, copper-based alloys and nickel-titanium (NiTi) alloys, are considered to have potential for commercial engineering applications. The copper based alloys, such as Cu-Zn-Al, Cu-Al-Ni, Cu-Zn-Si, Cu-Zn-Sn, Cu-Sn, Cu-Zn, Mn-Cu, have a more extensive range of potential transformation temperatures and they are made of relatively inexpensive materials. They have lower processing costs than NiTi SMAs, partially because they can be melted and extruded in air instead of being processed in a vacuum. However, in spite of higher costs and more complicated fabrication, NiTi alloys have many unique characteristics, compared to the other alloys, that make them maybe the only practical shape memory alloys. The essential benefits of Niti alloys are the following [13, 6]:

- high shape memory strain, up to 8% (copper-base alloys up to 5%)
- very good shape memory/superelastic characteristics (only after proper thermomechanical treatments)
- low elastic anisotropy
- high ductility (60% cold working possible)
- excellent corrosion and abrasion resistance
- better thermal stability and ageing properties
- biomedical compatibility
- potentiality to amorphisation
- high damping capacity
- relatively high electrical resistance.

The mechanical properties of shape-memory alloys are principally determined by their composition, which allows them to be tailored to suit many different applications. Table 6.1 lists some of the typical properties of these alloys, manufactured by medical technologies n.v. (formerly Advanced Materials and Technologies, AMT) [www.amtbe.com].

Table 6.1 Properties of different shape memory alloys (by medical technologies n.v.)

	Ni–Ti	Cu–Zn–Al	Cu–Al–Ni
Melting temperature (°C)	1,300	950–1,020	1,000–1,050
Density (g cm^{-3})	6.45	7.64	7.12
Resistivity (μΩ cm)	70–100	8.5–9.7	11–13
Thermal conductivity (W cm^{-1} per °C)	18	120	30–43
Young's modulus (GPa)	83 (austenite) 26–48 (martensite)	72 (beta phase) 70 (martensite)	85 (beta phase) 80 (martensite)
Yield strength (MPa)	195–690 (austenite) 70–140 (martensite)	350 (beta phase) 80 (martensite)	400 (beta phase) 130 (martensite)
Ultimate tensile strength (MPa)	895	600	500–800
Shape-memory strain (% maximum)	8.5	4	4
Transformation range (°C)	–200–110	<120	<200
Transformation hysteresis (°C)	30–50	15–25	15–20

Fabrication of shape memory alloys

SMA alloy materials can be fabricated into bars, strips, fibres or wires, tubing, foils, thin films, particles and even porous bulks. In the next few paragraphs the aspects of SMA fabrication (melting, basic fabrication, secondary processing methods, finishing technologies) are based mainly on the fabrication of NiTi.

Molten Nitinol is highly reactive and must be processed in a vacuum. Both vacuum induction melting (VIM) and vacuum consumable arc melting (VAR) processes are commonly used for production [14]. The most important properties of SMA are those two transformation temperatures from martensite to austenite and vice versa. They can be altered by changing the composition of the alloy. At certain concentration levels as tiny as one weight percent deviation, variations in Ni or Ti content can result in about a 100 °C shift in transformation temperatures. The transformation temperatures can be measured by monitoring practically any property of the alloy, such as electrical resistance, or stress-strain in a standard tensile test at temperatures across the transformation, but the most accurate means is differential scanning calorimetry (DSC) [6, 14].

After melting, the NiTi ingot is usually forged and rolled into a bar or a slab at elevated temperatures around 800 °C where the alloy is easily workable. The final dimensions with the desired physical and mechanical properties are obtained by cold working and appropriate heat treatments. Cold working of NiTi is quite challenging due to multiple reductions and frequent inter-pass annealing at 600–800 °C [14]. NiTi can be machined using conventional techniques such as milling, turning, drilling, grinding, sawing and water jet cutting. Laser and electro-discharge machining and photochemical etching processes are used to fabricate NiTi components such as tubular stents, baskets and filters. Various powder metallurgy processes have also been developed for NiTi. Porous Nitinol has attracted recent attention to its potential as an implant material [14].

Corrosion resistance is significantly affected by methods of surface preparation. After different heat treatments the surface of NiTi contains oxide layers, which can be removed by mechanical means, such as grit blasting and polishing, or by chemical etching. Mechanically polished surfaces, although they can be highly smooth, appear to be most susceptible to corrosion attack while the chemically etched surfaces appear to be the most resistant. Electro-polishing alone does not sufficiently enhance corrosion resistance [14].

NiTi can be quite easily soldered using halogen-based fluxes. It can also be welded to itself by using CO_2 laser, but joining NiTi to dissimilar metals is significantly more challenging. Welding NiTi to stainless steel is especially difficult due to the formation of brittle intermetallic compounds [14]. Thermal spray is a conventional thick film coating technology. NiTi coating can be applied by plasma spraying or physical vapour deposition [15] The process has also been used to fabricate NiTi foils and thin wall mill products.

More recently, thin film SMA has become a promising material in the field of micro-electro-mechanical system (MEMS) applications (such as micro-grippers, micro-pumps, micro-mirror, sensors and actuators). Thin film can be patterned with standard lithography techniques and fabricated in a batch process. Thin film SMA has only a small amount of thermal mass to heat or cool, thus the cycle (response) time can be reduced substantially and the speed of operation may be increased significantly. In thin film applications the fabrication of NiTi actuators have been made by first depositing NiTi on silicon, glass or polymeric substrates by sputter deposition. Commercial devices consisting of Nitinol film on silicon substrate are then fabricated by photolithographic techniques [14, 31].

SMA applications

The first successful industrial application of a shape memory alloy took place in 1970, when *Cryofit* tube coupling was demonstrated as a part of high-pressure hydraulic system on a US Navy F-14 fighter aircraft. In the following years, these demonstrations led to the production of over a million couplings [16, 17]. Since then the range of applications for SMAs has been increasing and one major area of expansion has been medicine. However, despite thousands of patents issued for every conceivable application for shape memory alloys, the list of the truly successful commercial devices is quite short. In SMA applications, superelastic devices have been the most significant so far in both material consumption and commercial value [16, 17].

The bulk shape-memory alloys exhibit large strokes and forces but suffer from a slow response. The bandwidth is usually near 1 Hz, which limits the material's applicability in many situations. The bandwidth limitation is due to the relatively slow cooling processes related to surface area-to-volume ratios. SMA thin films provide a small amount of thermal mass to be cooled, and hence the cycle lifetime can be decreased substantially.

6.3 Shape memory ceramics

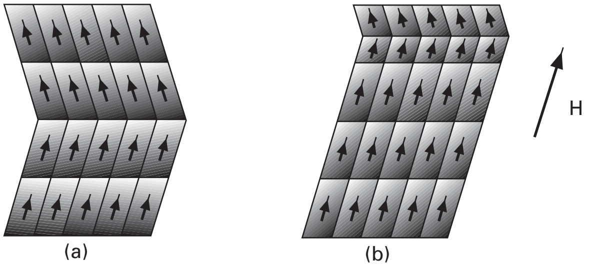
Shape memory effects can also be found in ceramic materials. Shape memory ceramics (SMC) can be categorised as viscoelastic, martensitic, ferroelectric or ferromagnetic depending on their activation mechanism [1]. Shape memory ceramics (SMC) can tolerate much higher operating temperatures than other shape-memory materials, but their recoverable strain is quite small. On the other hand, the actuation by electric field, for instance, can be much faster than by heat.

6.4 Magnetic shape memory materials

The principle of magnetic shape memory (MSM) alloys was presented in 1996 by Ullakko *et al.* [18]. MSM alloys belong to a novel group of shape memory materials that can change their shape in less than a millisecond and generate up to 10% strain when exposed to a magnetic field. Today there are several different alloy types, such as Ni-Mn-Al, Ni-Mn-Al, Fe-Pd, Co-Ni-Ga, Ni-Co-Al, but the most promising material seems to be Ni-Mn-Ga [19–20].

The MSM mechanism is based on the martensite twin boundary motion driven by the external magnetic field, when the material is in complete martensitic state [21]. Magnetic materials, even without an external magnetic field, are characterised by local magnetic moments, which have a certain preferable direction (the so-called easy direction) in respect to the crystal lattice. If the easy direction and the twin direction in a twinned microstructure are parallel, the lattice orientations of the twin variants are different and therefore the magnetisation directions also differ, as shown in Fig. 6.4(a) [22].

When an external magnetic field is applied, the magnetic moments try to align in the field direction. However, if the energy required to rotate the magnetisation out of the easy direction (the *magnetic anisotropy energy* MAE) is higher than the energy required to move a twin, it is energetically more favourable to move the twin boundaries instead of rotating the magnetisation. The fraction of twins, where the easy axis is in the direction of the field, will grow at the expense of the other twin variants. This process



6.4 (a) Magnetic moments without the external field; (b) redistribution of the variants in an applied field [22].

results in large shape changes as shown schematically in Fig. 6.4(b) [22].

There are two basic requirements for the appearance of the MSM effect. First, the material should be (ferro)magnetic and exhibit martensitic transformation, and second, the magnetic anisotropy energy should be higher than the energy needed to move the twin boundaries. Also from the practical applications point of view the material should be in its martensitic phase at room temperature [22].

MSM materials can be made to change their shape in different ways, to elongate axially, bend or twist. So far, actuators developing linear axial motion are the most common. The characteristics of present MSM actuators are [20]:

- large strokes and large forces
- high frequency operation (rise time is normally less than 0.2 ms; it is limited by flux generation and the inertia of the moving mass rather than MSM mechanism of the material)
- electromechanical hysteresis produce losses in MSM material, it also complicates the control of some positioning system applications
- hysteresis increases vibration-damping capacity of the MSM material
- wide operating temperature range (between –70 °C and 100 °C)
- MSM actuators can operate long times at high frequencies without significant fatigue of the actuating element (> 200 million cycles).

One of the pioneering companies in the field of magnetic shape memory research and applications is Adaptamat Ltd in Finland. It produces commercial MSM materials and different types of actuators.

6.5 Shape memory polymers and gels

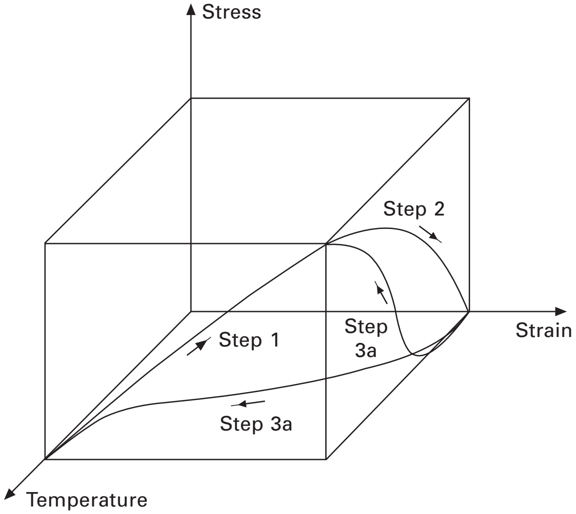
6.5.1 General properties of shape memory polymers

Shape memory polymers (SMPs) were first introduced in 1984 in Japan. Shape memory behaviour can be observed for several polymers that may differ significantly in their chemical composition. In SMPs, the shape memory effect is not related to a specific material property of single polymers; it rather results from a combination of the polymer structure and the polymer morphology together with the applied processing and programming technology [2]. Just like SMAs, the most common stimulus in SMP applications is heat. However, there is much ongoing research on systems, which may respond also to other stimuli, such as UV light, water, pH, electric or magnetic field. Some success has been reported on light and water induced SMPs [3, 5].

A thermally induced polymer undergoes a shape change from its actual, deformed temporary shape to its programmed permanent shape after being heated above a certain activation temperature T_{trans} [2]. SMPs are characterised by two main features, triggering segments having the thermal transition T_{trans} within desired temperature range, and cross-links determining the permanent shape. Depending on the kind of cross-links, SMPs can be thermoplastic elastomers or thermosets [29].

Segmented polyurethane thermoplastic SMPs have two separated molecular phases, a hard segment and a soft segment, with different glass transition temperatures, $T_{g,hard}$ being higher than $T_{g,soft}$. The polymer can be processed using conventional techniques (injection, extrusion, blow moulding) to desired shapes. During the processing stage, the material is at or above the melting temperature, T_{melt}, and all of the polymer chains have high degrees of mobility. Once the material cools down to $T_{g,hard}$, the configuration of the hard segments is 'stored' by physical cross-links. However, at temperatures between $T_{g,soft}$ and $T_{g,hard}$, the soft segments still allow the material to deform to a temporary shape while the physical cross-links of the hard segments store strain energy. Below $T_{g,soft}$, the material is completely glassy, and will hold a deformed shape without external constraint. When the material is heated back above $T_{g,soft}$, the soft segments are too mobile to resist the strain energy stored in the bonds of the hard segments, and an unconstrained recovery from the temporary deformed shape to the original 'stored' shape occurs. At temperatures higher than $T_{g,hard}$, the physical cross-links of the hard segments are released, thus erasing the 'memory' of the polymer. As the polymer is a three-dimensional network, a SMP can fully recover near 100% strain in all three dimensions [23].

The typical representation of the thermomechanical cycle of an SMP is shown in Fig. 6.5 [24]. Before starting the cycle the SMP is first heated to $T_{g,soft.}$. The first step of the cycle describes the high-strain deformation of the SMP to the desired temporary shape. During step 2 the material is cooled under constraint to hold the deformation. The stress required to hold this earlier deformed shape diminishes gradually to zero as temperature decreases. The temporary shape is now 'locked' and the constraint can be removed. In the final step of the cycle, the SMP is subjected to a prescribed constraint level and then heated again towards $T_{g,soft}$. In Fig. 6.5, the two limiting cases

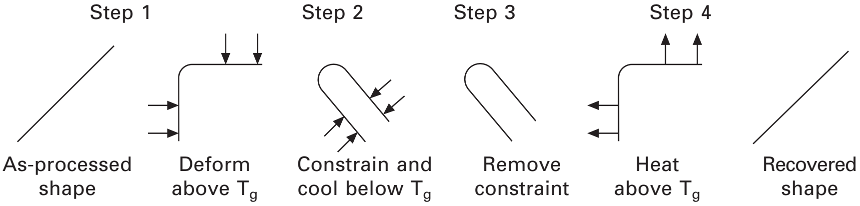


6.5 Stress-strain behaviour of different phases of NiTi at constant temperature.

of constraint are shown, namely a constrained recovery (step 3a) and an unconstrained recovery. Constrained recovery implies the fixing of the pre-deformation strain and the generation of a gradually increasing recovery stress. Unconstrained recovery implies the absence of external stresses and the free recovery of the induced strain. With the increase of temperature, the strain is gradually recovered. After the shape recovery step, the remaining strain is called residual strain. Recovered strain is defined as the pre-deformation strain minus the residual strain [24]. Figure 6.6 further illustrates the material's behaviour during an unconstrained shape recovery [25].

The benefits of SMPs over SMAs [1–3, 14, 23–27]:

- much lower density
- very high shape recoverability (maximum strain recovery more than 400%)



6.6 Schematic picture of the idealised thermo mechanical cycle leading to unconstrained strain recovery for a shape memory polymer [25].

- the shape recovery temperature can be engineered to occur over a wide range
- the recovery temperature can be customised by adjusting the fraction of the hard and soft phases
- less complicated (and more economical) processing using conventional technologies
- fast programming process
- some polymer networks are also biocompatible and biodegradable.

Drawbacks of SMPs:

- low recovery time
- low recovery force; SMP's ability to generate a 'recovery' stress under strain constraint is limited by their relatively lower stiffness, the shape-recovery property is lost when rather a small amount of stress (<4 MPa) is applied to the polyurethane components [1]. However, the stiffness and recovery stress of shape memory polymers can be substantially increased, at the expense of recoverable strain, by the inclusion of hard ceramic reinforcements [27].
- Polyurethane SMP may lose its shape fixing capability after being exposed to air at room temperature (about 20 °C) for several days. It can, however, fully regain its original properties after being heated up to its melting temperature [28].

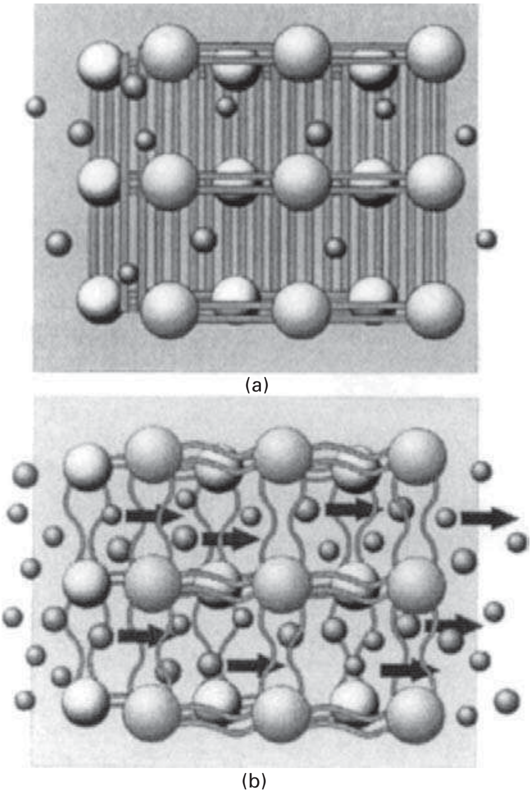
6.5.2 Applications of shape memory polymers

In literature and other media a large number of potential applications of shape memory polymers have been presented to suit various products in almost every aspect of daily life: industrial components like automotive parts, building and construction products, intelligent packing, implantable medical devices, sensors and actuators, etc. Yet, only a few shape memory polymers have so far been brought to commercial markets, and the number of implemented applications is still very small. SMPs are used in toys, handgrips of spoons, toothbrushes, razors and kitchen knives, also as an automatic choking device in small-size engines [30]. The main reason for the lack of 'killer applications' is most likely the fact that so far SMPs are suitable only for applications where free recovery or very low recovery force meets the requirements.

One of the most well known examples of SMP is a clothing application, a membrane called Diaplex. The membrane is based on polyurethane based shape memory polymers developed by Mitsubishi Heavy Industries. A part of the membrane is an ultra-thin nonporous polymer. Diaplex takes advantage of Micro-Brownian motion (thermal vibration) occurring within the membrane when the temperature rises above a predetermined activation point. As a result of this motion, the molecules form free spaces (micropores) in the membrane, which allows water vapour and body heat to escape (see Fig. 6.7). Because permeability increases as the temperature rises, the membrane is able to respond intelligently to changes in the wearer's environment and body temperature. Water vapour inside the garment is absorbed before it has a chance to condense. The absorbed water vapour is conducted into and diffused throughout the membrane and then emitted from the surface of the membrane [31].

Among the few suppliers making shape memory polymers are companies such as:

- *Mitsubishi Heavy Industries* (polyurethane based shape memory polymers – e.g. Diaplex)



6.7 (a) At low temperatures the polymer molecular chains form a continuous surface that restricts the loss of body warmth by stopping the transfer of vapour and heat. (b) At increasing temperatures the molecular configuration changes resulting in the formation of free space. This allows the transfer of heat and vapour from perspiration and helps to prevent discomfort and clamminess within the garment.

- *Composite Technology Development* (CTD) (Elastic Memory Composite (EMC) materials, shape memory thermosets)
- *CRG Industries LLC*, Veriflex™ shape memory thermosets, Veritex™ dynamic composites (Veriflex™ resin is used as the matrix)
- *The Polymer Technology Group Inc.* Calo•MER™ shape-memory thermoplastics
- *Bayer MaterialScience,* shape-memory thermoplastics
- *MnemoScience GmbH*, biodegradable thermoplastic shape memory polymers, etc.

6.5.3 Shape memory gels

Smart polymeric gels have an ability to react to infinitesimal changes in their environmental conditions by considerable volume changes, swelling or shrinkage. Volume changes can be triggered besides temperature also by a variation in the pH value, the ionic strength, biochemical element or the quality of the solvent. For certain gels the triggering stimulus can also be light or electric field or stress, depending upon the precise structure of the gel. The main negative aspect of gels is their poor mechanical stability [1, 2].

Gels are capable of conversion between chemical energy and mechanical work. By undergoing phase transitions, which are accompanied by reversible, continuous or discrete volume changes by three orders of magnitude, the gels can provide actuating power capacities comparable to that of human muscles [1].

6.6 Future prospects of shape memory materials

The potential future benefits of shape memory materials, their smart structures and systems, seem to be remarkable in their scope. The research on smart materials is growing all over the globe. However, shape memory materials do have their shortcomings to be overcome before their engineering significance is more widely recognised in the industrial world.

Within shape memory alloys there are problems mainly in the engineering and modelling aspects; fabrication and processing of high-quality and lower-cost materials. We need to understand the still unclear issues like hysteresis and ageing effects better. In addition, scientific research is required to get answers to a few ‘mysteries’, for example, if there is a common microscopic origin for all the martensitic transformations, and what the relationships between electronic structure and the competing martensite structures are [13].

Advancements in process development, especially in NiTi processing, allow SMAs to break into cost-sensitive commercial volume markets. The medical device market can tolerate higher cost but has a strict demand for superb quality and consistency. Thin film technology is about to become widely commercialised; process stability and quality control on thin film properties will probably attract far more attention and awareness. Thin film alloy bandwidths are reaching from 100 Hz to the theoretical predictions of the 1 kHz limit. These large bandwidths, in conjunction with large stress and strain output, provide films producing enormous values of power per unit mass. More and more compliant mechanisms are being developed using MEMS process technology. The relatively large power provides unique opportunities for small-scale industrial and biomedical applications (e.g. miniature motors, heart valves and drug delivery systems) [32].

The future applications of magnetic shape memory alloys will be broadened from actuators to new application areas, such as fluidics, vibrators, couplers, positioning devices, sensors and generators. Complicated mechanical structures can be simplified by using MSM materials. One future vision is a sewing machine: a traditional sewing machine has a rotating electric motor and a large number of parts in a rather complicated mechanical transmission system, although the desired motion of the needle is up and down. A sewing machine based on MSM technology could consist of an electromagnet (coil) and a needle made of MSM material.

Much future effort with SMPs will probably be applied to increasing the recovery force of SMPs. One possible way of doing this is reinforcing the polymer matrix with carbon or glass fibres or ceramic filler particles. [24, 25] The two-way shape-memory effect and stimuli other than temperature, such as light or electromagnetic fields, will play a major role in future research. Degradable shape-memory polymers will provide interesting advantages over metal implants, because much of today's follow-on surgery in removing the implants can thus be avoided. SMP-based biological micro-electromechanical systems (Bio-MEMS) are also expected to be a potential medical application. On the other hand, SMP micro-grippers have potential use also in industrial applications where objects must be manipulated in unreachable locations in micro-system assembly.

In the history of man, textiles were the driving force to industrialisation – now it seems that smart textiles and intelligent clothing can play an important role again when developing smart materials for all-round applications.

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7

Temperature sensitive shape memory polymers for smart textile applications

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7.1 Introduction

Material scientists predict a prominent role in the future for intelligent materials [1]. Environmentally responsive materials that respond to the external conditions and exhibit various functions are called intelligent [2–3] or smart materials. Research on such materials is actively beginning in various fields. Shape memory materials are one kind of such smart materials, which have the ability to remember their original shapes. When the material deforms into a temporary shape it returns to its original shape by external stimuli. This feature, known as the shape memory effect, was first observed in samples of gold-cadmium in 1932 and 1951, and in brass (copper-zinc) in 1938.

It was not until 1962, however, that William J. Buehler and coworkers at the Naval Ordnance Laboratory (NOL) discovered that nickel-titanium showed this shape memory effect [4]. Shape memory polymers (SMPs) are one type of shape memory materials defined as polymeric materials with the ability to sense and respond to external stimuli by returning to a predetermined shape. Polymer such as polynorbornene, trans-polyisoprene, styrene-butadiene copolymer, crystalline polyethylene, some block copolymer, ethylene-vinyl acetate copolymer and segmented polyurethane, etc., have been discovered with shape memory effect. Organic shape memory polymers have a lower recovery force than do shape memory alloys but offer easier processability, light weight, lower production costs, biocompatibility and color variation [5].

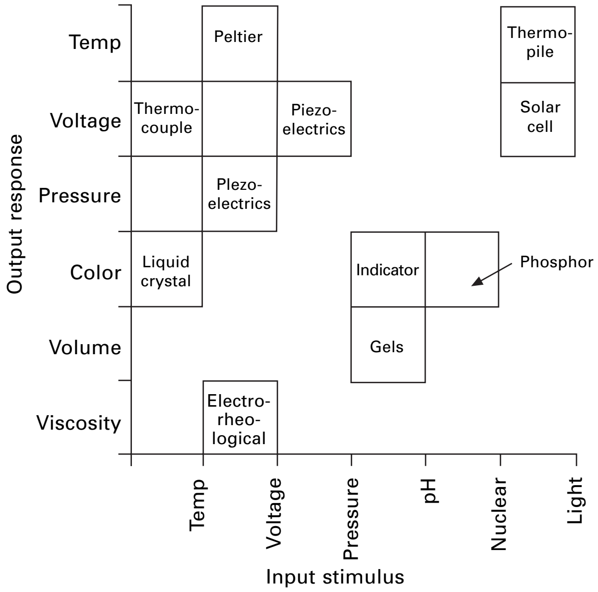
Compared with shape memory alloys, SMPs have better potentiality for textile and clothing, and related products. In the case of SMAs, mechanical properties can be adjusted only within a limited range and the maximum deformation that they can undergo is about 8%. In contrast, shape memory polymers (SMPs) have easy shaping, high shape stability, and adjustable transition temperature. Both the shape memory effect and the elasticity memory system effect of shape memory polymers make them a useful candidate for today's intelligent material systems and structures [6]. Here we present a review of temperature sensitive shape memory smart polymeric materials;

such materials can respond to changes in the temperature fields in their environment and make a desirable response for smart textiles.

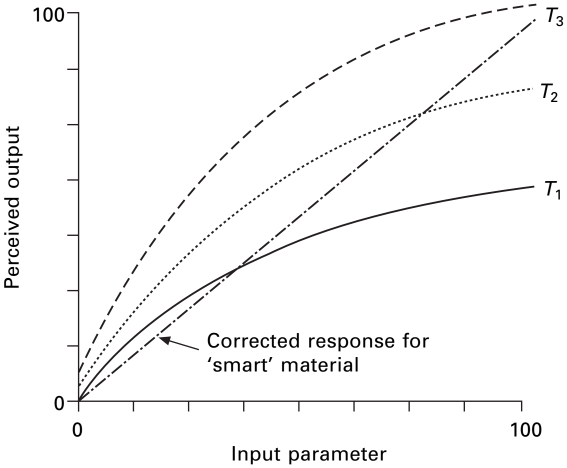
7.2 A concept of smart materials

The term ‘smart materials’ is much used and more abused. All materials are responsive. Whether or not they are smart materials is a different question. The responsivity is often useful and forms the basis of transducer technology. Such material systems do exist and involve a spectrum of constituents. A simple pressure transducer that produces a voltage dependent upon the input pressure in a direct one-to-one relationship could never be regarded, as ‘smart’. However, a pressure transmitter incorporating a thermocouple that measures both temperature and apparent pressure and corrects the apparent pressure taking due note of the sensor’s temperature coefficient could be regarded as smart [7].

Figure 7.1 illustrates the functions of a range of transducer materials and indicates how their input/output characteristics may be summarized in a simplistic graphical form. However, returning to our original definition, there is no ‘smartness’ here since the output has the same, or sometimes a larger, information content than the input. To engender smartness we need responsivity to a second variable, illustrated conceptually in Fig. 7.2. If the



7.1 Response of some sensor materials. These materials are often referred to as ‘smart’, but are they? (Adapted with permission from Smart Structures and Materials, B. Culshaw, © 1996, Artech House Publisher [7]).



7.2 The response of a 'smart' material. The uncorrected response is a function of the parameter T, but after correction in the material, an unambiguous output is obtained, independent of T. (Adapted with permission from Smart Structures and Materials, B. Culshaw, © 1996, Artech House Publisher [7]).

material can be designed to produce a specific response to a combination of inputs, then it will fulfill the smartness requirements. The term 'smart' describes material that can sense changes in its environment and make a useful or optimal response by either changing its material properties, geometry, mechanical or electromagnetic properties. The smart materials are now one of the most studied fields, because of their ability to change their physical and thermomechanical properties when it is necessary. The concept of intelligent/smart materials implies substances or materials which are able to appropriately respond to changes of external factors by changing their structure and functions [8]. The basic concept of smart materials is that they have their own sensor which is able to change the characteristics of the materials. Smart materials are expected to adapt to their environment and provide a useful response to changes in the environment [9]. The environment may include fluid loading, material damping, the effect of the backing structure and changes in both the structure and the environment. In all cases, smart materials should sense the change and make a useful response. And overall, the intelligent materials will build themselves.

7.3 Shape memory polymer and smart materials

A material which changes one of its property coefficients in response to an external stimulus, and where this change in coefficient can be used to control the stimulus is called a smart material [10]. This definition is then consistent with the behavior of a shape memory polymer (SMP), with the potential for application as a smart material and also as a new functional material. For example, the well-known use as a control for knotting by a smart suture made with shape memory polymer which ties itself into a perfect knot where access is limited [11]. Its self-knotting action occurs when it is heated a few degrees above normal body temperature. At the start, a key characteristic of polymeric materials, which are good candidates for development into smart intelligent materials, is the ability to change properties, such as structure or composition, and function in a controlled response to a change in environment or operating conditions. The next level is the promise for development of some level of built-in intelligence, such as graded reaction to stimuli and ability to recognize or discriminate shapes or forms [12].

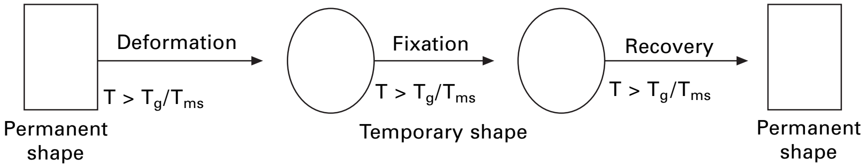
Stimuli sensitive polymers (SSPs) or shape memory polymers (SMPs) yield intelligent textiles that exhibit unique environmental responses. The molecular design of SSPs [13] facilitates phase change behavior in response to environmental stimuli and allows SSP textiles to change structures and properties. SSPs yield fabrics with such properties as air permeability, hydrophilicity, heat transfer, shape, and light reflectance that are responsive to such environmental stimuli as temperature, pH, moisture, light, and electricity. Shape memory polymers (SMPs) offer greater deformation capacities, easier shaping, and greater shape stability, and small changes to the chemical structure and composition of SMPs result in a wide variety of transition temperatures and mechanical properties.

7.3.1 Principle of temperature sensitive shape memory polymer

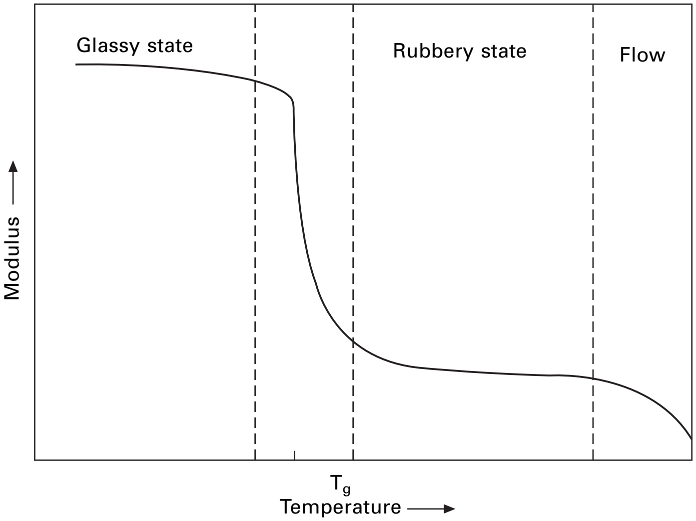
Shape-memory materials are stimuli-responsive materials. They have the capability of changing their shape upon application of an external stimulus. Shape memory may be triggered by heat, light, electric field, magnetic field, chemical, moisture, pH and other external stimuli [5–6]. Change in shape caused by a change in temperature is called a thermally induced shape-memory effect. These are materials which are stable at two or more temperature states. While in these different temperature states, they have the potential to be different shapes once their 'transformation temperatures' (Tx) have been reached. Shape memory alloys (SMAs) and Shape Memory Polymers (SMPs) are materials with very different shape changing characteristics. While exposed to their Tx, devices made from SMAs have the potential to provide force such as in the case of actuators. Devices made from SMPs in contrast, while exposed to their Tx, provide mechanical property loss as in the case with releasable fasteners. The shape memory polymers described in this chapter are all thermosensitive shape memory polymers.

Temperature sensitive shape memory polymers are a special class of adaptive materials which can convert thermal energy directly into mechanical work. This phenomenon, known as the shape-memory effect (SME) occurs when one of these special polymers is mechanically stretched at low temperatures, then heated above a critical transition temperature, which results in the restoration of the original shorter 'memory' shape of the specimen [14]. The proposed theory expresses well the thermomechanical properties of thermoplastic polymer, such as shape fixity, shape recovery, and recovery stress [1]. The mechanism of shape memory behavior with temperature stimuli can be shown as outlined in Fig. 7.3. These materials have two phase structures, namely, the fixing phase which remembers the initial shape and the reversible phase which shows a reversible soft and rigid transition with temperature.

At temperatures above the glass transition temperature (T_g), the polymer achieves a rubbery elastic state (Fig. 7.4) where it can be easily deformed without stress relaxation by applying external forces over a time frame $t < \tau$, where τ is a characteristic relaxation time. When the material is cooled below its T_g, the deformation is fixed and the deformed shape remains stable. The pre-deformation shape can be easily recovered by reheating the material



7.3 Typical temperature stimulating shape memory behaviors.



7.4 Temperature dependency elasticity of thermoplastic polymer.

to a temperature higher than the T_g [15]. Therefore, admirable shape memory behavior requires a sharp transition from glassy state to rubbery state, a long relaxation time, and a high ratio of glassy modulus to rubbery modulus. The micromorphology of SMPs strongly affects its mechanical properties. There are many factors that can influence these SMPs: chemical structure, composition, and sequence-length distribution of the hard and soft segment in segmented polymer, overall molecular weight and its distribution. An elastomer will exhibit a shape-memory functionality if the material can be stabilized in the deformed state in a temperature range that is relevant for the particular application. The shape is deformed under stress at a temperature near or above T_g or the segment crystal melting temperature, T_{ms}. The deformed shape is fixed by cooling below T_g or T_{ms}. The deformed form reverts to the original shape by heating the sample above T_g or T_{ms}.

7.3.2 Architecture of the shape memory polymer-network

Shape memory effect is not related to a specific material property of single polymers; it rather results from a combination of the polymer structure and the polymer morphology. Shape memory behavior can be observed for several polymers that may differ significantly in their chemical composition and structure. The shape memory polymers that show a thermally induced shape-memory effect are network structure. The netpoints, which can have either a chemical or physical nature, determine the permanent shape. The net chain shows a thermal transition in the temperature range which the shape-memory effect is supposed to trigger. Segmented polymer with shape-memory effect properties requires a minimum weight fraction of hard-segment-determining blocks to ensure that the respective domains act as physical netpoints [1]. Formation of a network structure with rigid point/segments (fixed phase) and amorphous/flexible segment/regions (reversible phase) are the two necessary conditions for their good shape memory effect [16]. In general, interpolymer chain interactions are so weak that one-dimensional polymer chains cannot keep a certain shape above Tg.

To maintain a stable shape, polymer chains should have a three-dimensional network structure. Interpolymer chain interactions useful for constructing the polymer network are crystal aggregate or glassy state formation, chemical cross-linking, and chain entanglement [5]. The latter two interactions are permanent and used for constructing the original shape. The other interactions are thermally reversible and used for maintaining the transient shapes. This can be reached by using the network chains as a kind of molecular switch. For this purpose the flexibility of the segments should be a function of the temperature. One possibility for a switch function is a thermal transition (T_{trans}) of the network chains in the temperature range of interest for the particular applications. The crystallites formed prevent the segments from spontaneously recovering the permanent shape that is defined by the netpoints. The permanent shape of the shape memory network structure is stabilized by covalent netpoints, whereas the permanent shape of the shape memory thermoplastics is fixed by the phase with the highest thermal transition at T_{perm} [1].

7.4 Some examples of shape memory polymer for textile applications

Many polymers have been discovered with shape memory effects. Some of them suitable for textiles applications are shown in Table 7.1 along with physical interactions used for memorizing the original and transient shapes of the polymers.

7.4.1 Polynorbornene

Norsorex is linear, amorphous polynorbornene **30** developed by the companies CdF Chemie/Nippon Zeon in the late 1970s. The molecular weight is as high as 3 million [20–21]. The polymer contains 70 to 80 mol% *trans*-linked norbornene units and has a glass transition temperature between 35 and 45 °C [17–18]. The shape memory effect of this amorphous polymer is based on the formation of a physical cross-linked network as a result of entanglements of the high molecular weight linear chains, and on the transition from the glassy state to the rubber-elastic state [19]. The long polymer chains entangle

Table 7.1 Shape memory polymer and mechanisms [1, 5]

Polymers	Physical interactions	
	Original shape	Transient shape
Polynorbornene	Chain entanglement	Glassy state
Polyurethane	Microcrystal	Glassy state
Polyethylene/nylon-6 graft copolymer	Crosslinking	Microcrystal
Styrene-1,4-butadiene block copolymer	Microcrystal/Glassy state of polystyrene	Microcrystal of poly(1,4-butadiene)
Ethylene oxide-ethylene terephthalate block copolymer	Microcrystal of PET	Microcrystal of PEO
Poly(methylene-1, 3-cyclopentane) polyethylene block copolymer	Microcrystal of PE	Glassy state/micro-crystal of PMCP

each other and a three-dimensional network is formed. The polymer network keeps the original shape even above Tg in the absence of stress. Under stress the shape is deformed and the deformed shape is fixed when cooled below Tg. Above the glass transition temperature polymers show rubber-like behavior. The material softens abruptly above the glass transition temperature Tg. If the chains are stretched quickly in this state and the material is rapidly cooled down again below the glass transition temperature the polynorbornene chains can neither slip over each other rapidly enough nor become disentangled. It is possible to freeze the induced elastic stress within the material by rapid cooling. The shape can be changed at will. In the glassy state the strain is frozen and the deformed shape is fixed. The decrease in the mobility of polymer chains in the glassy state maintains the transient shape in polynorbornene. The recovery of the material's original shape can be observed by heating again to a temperature above Tg. This occurs because of the thermally induced shape-memory effect [19]. The disadvantage of this polymer is the difficulty of processing because of its high molecular weight [5].

7.4.2 Segmented polyurethane

Shape memory polyurethane (SMPU) is a class of polyurethane that is different from conventional polyurethane in that these have a segmented structure and a wide range of glass transition temperature (Tg). Segmented polyurethane is composed of three basic starting raw materials, these are (i) long chain polyol, (ii) diisocyanate and (iii) chain extender. Diisocyanate and chain extender form a hard segment. On the other hand long chain polyol is soft segment. These types of polyurethanes are characterized by a segmented structure (block copolymer structure) and the morphology depends on chemical composition and the chain length of the soft segment (block). The SMPU has a microphase separated structure due to the thermodynamic incompatibility between the hard and soft segment. Hard segments can bind themselves via hydrogen bonding and crystallization, making the polymer solid below melting point temperature. Reverse phase transformation of soft segment is reported to be responsible for the shape memory effect.

The shape memory effect can be controlled via the molecular weight of the soft segment, mole ratio between soft and hard segment, and polymerization process [20]. If a SMPU is cooled from above Tg to a temperature below Tg, in the presence of a mechanical load, and after removal of load, significant deformation anywhere in the range of 10–200% becomes locked into the polymer. Phase-transition temperature of shape memory polyurethane is a little higher than the operating tempeaure. A large drop of modulus and an enhanced micro-Brownian motion on heating through glass transition or soft segment crystal melting temperature can be used in the molecular design of the shape memory behavior [21–22]. Shape memory characteristics of the segmented polyurethanes having crystallizable soft segments are closely related to the temperature-dependent dynamic mechanical properties of the materials [21, 23]. A large glassy state modulus led to large shape recovery upon heating and standing at high temperature. On the other hand, high crystallinity of the soft segment regions [21, 24] at room temperature and the formation of stable hard segment domains acting as physical crosslinks in the temperature range above the melting temperature of the soft segment crystals are the two necessary conditions for a segmented copolymer with shape memory behavior.

The response temperature of shape memory is dependent on the melting temperature of the soft segment crystals. The final recovery rate and the recovery speed are mainly related to the stability of the hard segment domains under stretching and are dependent on the hard segment content. Control of hard segment content is important in determining the physical properties of shape memory polyurethane. The amount of hard segment rich phase would affect the ratio of the recovery, that is, the low content leads to the recovery of the deformed specimen being incomplete [25]. The recovery rate would be influenced by the modulus ratio and the size of the dispersed phase in the micromorphology.

Polyurethane with 20 or 25% of hard segment content could not show shape recovery due to weak interaction or physical cross-link. On the other hand with 50% hard segment did not show shape recovery due to the excess interaction among the hard segment and the resulting rigid structure. The maximum stress, tensile modulus and elongation at break increased significantly at 30% hard segment content, and the highest loss tangent was found typically at the same composition. Finally, 80–95% of shape recovery was obtained at 30–45 wt% of hard segment content [26]. The typical textile applications of SMPU are as fibre, coating, lamination, etc.

7.4.3 Polyethylene/nylon 6 graft copolymer

High density polyethylene ($\rho = 0.958$ g/cm^3) grafted with nylon-6 that has been produced in a reactive blending process of PE with nylon-6 by adding maleic anhydride (bridging agent) and dicumyl peroxide shows shape memory properties [27]. The nylon contents in the blends are in the range from 5 to 20 wt%. The maleated polyethylene/nylon 6 blend specimens are able to show good shape memory effect under normal experimental conditions. An elastic network structure is formed in these M-PE/nylon 6 blends, and the nylon domains (domain size less than 0.3 μm) dispersed in the PE chains in the matrix region. The high crystallinity of polyethylene segments at room temperature and the formation of a network structure in these specimens are the necessary conditions for their good shape memory effect. The nylon domains, which serve as physical cross links, play a predominant role in the

Table 7.2 Shape memory properties of HDPE-g-nylon-6

Samples	Strain fixation (%)	Strain recovery (%)	Recovery temperature (°C)
Ir-PE	96.2	94.4	100.5
PE with 20 wt% nylon-6	98.6	96.6	120.3
PE with 15 wt% nylon-6	98.9	96.0	121.0
PE with 10 wt% nylon-6	99.5	96.0	121.3
PE with 5 wt% nylon-6	99.8	95.0	118.8

(Adapted with permission from Li *et al. Polymer*, 39 (26), 6929, © 1998, Elsevier [27]).

formation of a stable network structure for the graft copolymer. All the M-PE/nylon blend specimens exhibit typical good shape memory behavior, having final recovery rates, R_f, more than 95% and high recovery speeds comparable to those of low-density PE cross-linked by reaction with ionizing radiation (Ir-PE), the commercial sample with a high degree of chemical cross-linking. The response temperature of blend samples, around 120 °C, is closely related with the melting temperature of the PE crystals in these specimens. Strain fixity rates of around 99% and strain recovery rates between 95 and 97% have been determined for these graft copolymers for an elongation 100% (Table 7.2). Shape memory properties of PE-g-nylon-6 with fixed contents of DCP (0.08 phr) and MAH (1.5 phr) along with Ir-PE are given in Table 7.2.

7.4.4 Block copolymers

Some block copolymers with phase-separated structures show the following shape memory properties.

Styrene-1,4-butadiene block copolymer

The crystal transformation of semicrystalline styrene-butadiene block copolymer attributes the shape memory properties [28–29]. Phase separated block copolymer contain 34 wt% polystyrene (PS) and 66 wt% poly(1,4-butadiene). The melting temperature of the poly(1,4-butadiene) crystallites (around 80 °C) represents the switching temperature for the thermally induced shape-memory effect. Aggregate or glassy state formation in polystyrene segment is used to memorize the original shape. Thus, polystyrene supplies hard domain. The high glass transition temperature and microcrystal structure of polystyrene segments hinders the polybutadiene chains from slipping off each other upon stretching. Below 40 °C the poly(1,4-butadiene) domain becomes crystallized and the deformed shape is fixed. The shape again returns to the original one upon heating at around 80 °C, at which microcrystal in the poly(1,4-butadiene) domain melts. A strain recovery of 80% is observed upon application of maximum of strain (ε_m) of 100%.

Ethylene oxide-ethylene terephthalate block copolymer

Microphase separated segmented copolymer based on poly(ethylene oxide) and poly(ethylene terephthalate) (EOET) shows shape memory behavior [30–32]. Polyethylene terephthalate (PET) domain formed hard segment phase, on the other hand poly(ethylene oxide) (PEO) domain formed soft segment rich phase. Thermally stimulated deformation recovery (R_f) depends on the stability of the physical cross-links formed by the hard segment, and at the same time, is influenced by the length of soft segment. A long PEO length could undergo a larger extension without dislocation from the anchor nodes of the PET-domain crystal that act as physical cross-links in the formation of the PEO-segment network. On the other hand, a higher crystallizability of longer PEO chains can impose a higher retardation of the relaxation of extended chains. Longer PEO segments would have a higher crystallinity, and a large number of PEO segments would crystallize rather than going into amorphous phase. The soft segment crystallization determines the thermally stimulated deformation recovery temperature T_r and T_M. R_f certainly also depends on the hard segment content and the molecular weight of the soft segment in the EOET segmented copolymers. Physical cross-linking formed by the hard segments are very well aggregated and not destroyed by stretching. With the same soft segment length, the higher the hard segment content, the better the aggregate formation and the corresponding deformation recovery is higher (Table 7.3).

Poly(methylene-1,3-cyclopentane) polyethylene block copolymer

New metallocene catalyst systems used to synthesize poly(methylene-1,3-cyclopentane) (PMCP), by the cyclopolymerization of 1,5-hexadiene [33].

Table 7.3 Shape memory properties of EOET copolymer

Block length of PEO (M_w)	HS (%)	T_r (°C)	T_M(°C)	R_f(%)
4000	27.6	45	45.2	84
4000	32.0	44	43.9	85
6000	21.2	48	47.3	90
6000	25.7	46	46.5	92
10,000	16.5	55	54.5	93
10,000	21.8	53	52.7	95

(Adapted with permission from Luo *et al. Journal of Applied Polymer Science,* 64, 2433, 1997, © 1997 John Wiley and Sons Ltd. [31]).

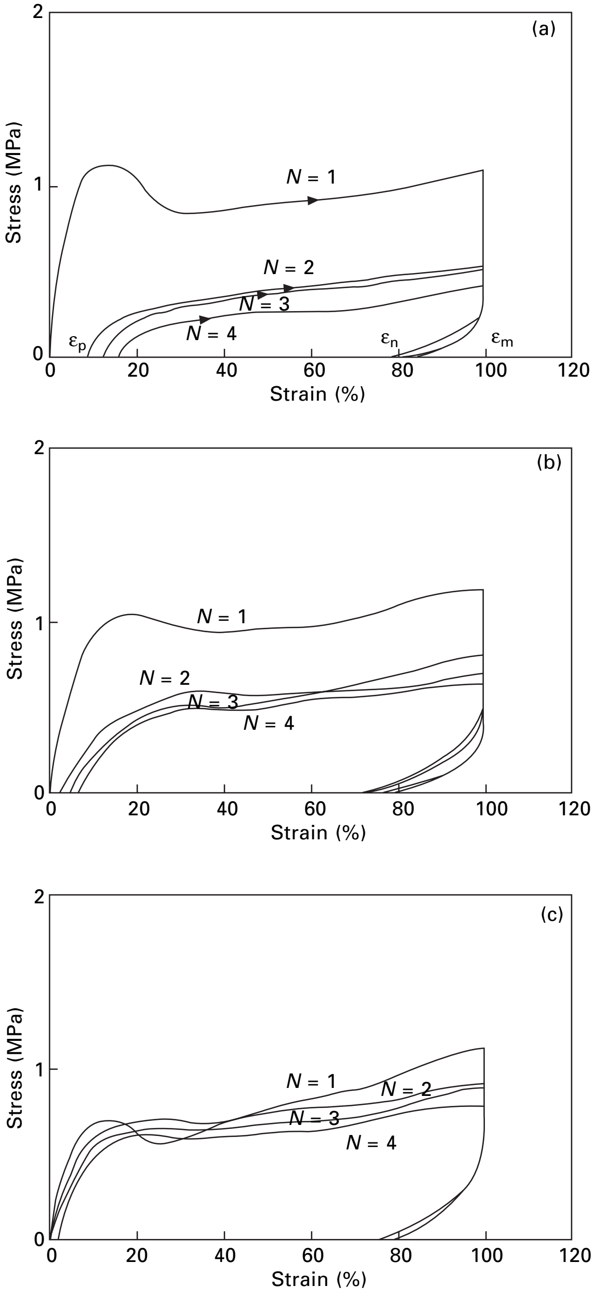
Block copolymer of PMCP and polyethylene obtained by addition polymerization of ethylene, i.e., after polymerization of 1,5-hexadiene shows a phase separated structure, where the PMCP domain act as a soft segment rich phase and the polyethylene domain as a hard segment phase. Crystal melting point of the hard segment was around 120 °C and that of the soft segment was nearly 64 °C. On the other hand, T_g of the soft segment was 5–10 °C. The sample was elongated at 45 °C in a rubbery state above T_g to 100% strain (ε_m), while maintaining the strain at ε_m, the sample was cooled to 25 °C and unloaded. Upon removing the constraint at 25 °C some recovery of the strain to ε_u occurs, because 25 °C is not far below but close to the T_g of the examined samples. The samples were heated to 85 °C, a temperature above the soft segment crystal melting temperature (T_{ms}), over a period of five minutes, and maintained at that temperature for the next ten minutes, allowing recovery from the strain. This completes one thermomechanical cycle (N = 1) leaving a residual strain ε_p where the next cycle (N = 2) starts. A shape fixity of more than 75% and shape recovery around 80% would obtained up to four thermomechanical cycles (Fig. 7.5).

7.5 Potential use of shape memory polymer in smart textiles

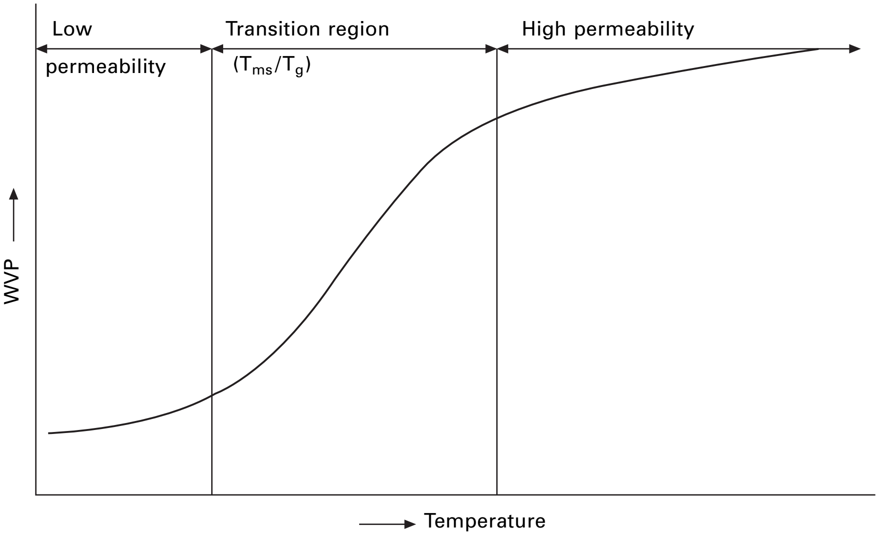
7.5.1 The use of the functional properties

Moisture permeability, volume expansion and refractive index vary significantly above and below T_g/T_{ms} according to the difference of the kinetic properties of molecular chains [34] between temperatures above and below T_g/T_{ms}. Temperature dependency of water vapor permeability is an important factor to be considered for the effective utilization of this type of smart materials. One of the applications of moisture permeability of a thin film is in sports wear. Moisture permeability is high above T_g/T_{ms} and low below T_g/T_{ms} (Fig. 7.6). For sports wear, the heat retaining property at low temperature and gas permeability at high temperature are excellent, yielding high quality for the sportswear. Imagine a coat that detected rain. It could change shape to keep the moisture out, but always be comfortable to wear. When the weather becomes cooler, it could change again to keep the wearer warm.

The shape-deformable matrix material contains an elastomeric, segmented block copolymer, such as a polyurethane elastomer or a polyether amide elastomer. The elastomeric polymer provides the force for dimensional change when the moisture-absorbing polymer softens and relaxes as a result of moisture absorption. The inclusion of a non-elastomeric polymer provides a degree of recovery when exposed to humidity. The activation process for the shape-deformable materials does not require substantially increasing the



7.5 Cyclic tensile behavior of (a) PMCP, (b) PMCP-PE1, and (c) PMCP-PE2 (elongated at 45 °C and recovered at 85 °C), N represents number of cycles, ethylene segment in PE1 and PE2 are 8.1 and 17.0% (wt%) respectively. (Adapted with permission from Jeong *et al.*, Polymer International, 51, 275, 2002, (c) 2002 SCI, John Wiley and Sons Ltd. [33]).



7.6 Temperature dependency water vapor permeability of shape memory polymers.

temperature of the materials, which helps in preventing leakage from the absorbent product. Also, by adjusting the chemical structure of the shape-deformable polymer, a specific polymer can be tailored to interact at a selected level of humidity. These kinds of shape memory materials would be applicable in disposable hygiene products, such as diapers, training pants, and incontinence products [35].

7.5.2 The use of changes of physical properties related to the phase transformation

Physical properties of materials are related to the crystal structure and microstructure of the involved phases. In spite of the diffusionless character of the phase transformation, the lattice parameter, crystal structure and microstructure of the parent phase and the reverse phase, differ significantly. As a consequence, during transformation, values of E-modulus, internal friction, electrical resistance, and hardness might change [36]. A typical example of changing phase change from temporary shape to permanent shape is suture. The technique of keyhole surgery minimizes scarring, speeds healing and reduces the risk of infection. However, it is extremely difficult to carry out delicate surgical procedures accurately in a confined space, such as implanting a bulky device or knotting a suture with the right amount of tension. In the latter case, if a knot is pulled too tight, necrosis of the surrounding tissue can occur, but if it is too loose, the incision will not heal properly and scar tissue develops [37].

Technology has developed a shape memory polymer that has been designed by MnemoScience to act as a smart suture that ties itself into a perfect knot. The suture's self-knotting action occurs when it is heated a few degrees above normal body temperature. The suture can therefore be used to seal difficult wounds where access is limited [11]. The material is a multi-block copolymer, in which block-building segments are linked together in linear chains. Specifically, the polymer they created contains a hard segment and a 'switching' segment, both with different thermal properties. One segment melts, or makes another kind of transition, at a higher temperature than the other. By manipulating the temperature and stress applied to the overall material, Langer and Leindlin end up with a material that forms a temporary shape at one temperature, and a permanent shape at a higher temperature. After increasing the temperature, the suture material shrunk, creating a knot with just the right amount of tension on the surrounding tissue. It is difficult to create such a knot in the confined spaces associated with endoscopic surgery. They demonstrated this by creating the first 'smart' degradable suture.

When SMPs change from glassy state to rubbery state, Young's modulus, tensile and elastic properties vary greatly, which would be useful for garments. For example, when the SMPs-based garments were washed at higher temperature or worn at body temperature, they could recover to the original state (wrinkle free). Shape memory fabrics regain the flatness of their appearance and retention of their creases after the fabrics have been immersed in hot water [6, 38].

7.6 General field of application

The recent advent of advanced 'intelligent' materials has opened the door for many useful applications in textile field. Although relatively few structures are presently built with such materials, the potential market for the application of these materials can be quite large. The unique properties of shape memory polymers resulting from thermally induced phase transformation has been exploited commercially to produce a variety of products. Due to the properties of shape memory polymers some suitable field of technical applications can be found. Shape memory polymers can be laminated, coated, foamed, and even straight converted to fibres. There are many possible end uses of these smart textiles, some of them are summarized in the following section.

7.6.1 Medical textiles

Smart fibre

The smart fiber made from the shape memory polymer designed by MnemoScience ties itself into a perfect knot. Features of the MnemoScience

[39] polymer material include its compatibility with body fluid, shape retention properties, retention of two shapes in memory, high shape fixity, high shape recovery, and its ability to form temporary and permanent shapes. The suture contracts to its permanent shape when heated and its self-knotting action occurs when it is heated a few degrees above normal body temperature. The suture therefore can be used to seal difficult wounds where access is limited. The other applications of smart fibers would be stents, and screws for holding bones together.

Surgical protective garments

Shape memory polymer coated or laminated materials can improve the thermo-physiological comfort of surgical protective garments, bedding and incontinence products because of their temperature adaptive moisture management features.

Other applications

Kimberly-Clark company in US Patent 6 627 673 [40] disclosed humidity-activated shape-memory materials. The materials could find particular application in disposable hygiene products, such as diapers, training pants and feminine care and incontinence products. They may be used, for example, in products containing a gatherable or elastic part. Stretching the humidity-responsive material forms the latent deformation. The humidity-responsive material contains at least one shape-deformable matrix material.

7.6.2 Outdoor clothing

Films of shape memory polymer can be incorporated in multilayer garments, such as those that are often used in the protective clothing or leisurewear industry. The shape memory polymer reverts within a wide range temperatures. This offers great promise for making clothing with adaptable features [41]. Using a composite film of shape memory polymer as an interliner in multilayer garments, outdoor clothing could have adaptable thermal insulation and be used as protective clothing.

The United States Army Soldier Systems Center developed [42] a wet/dry suit with a shape memory polymer membrane and insulation materials that keep the wearer warm in marine environments but do not inhibit perspiration on land. Molecular pores open and close in response to air or water temperature to increase or minimize heat loss. Apparel could be made with shape memory fiber. Forming the shape at a high temperature provides creases and pleats in such apparel [43] as slacks and skirts. Other applications include fishing yarn, shirt neck bands, and cap edges.

7.6.3 Casual clothing

Permeability of SMP coated or laminated fabrics changes as the wearer's environment and body temperature change to form an ideal combination of thermal insulation and vapor permeability for underwear and outerwear. When the body temperature is low, the fabric remains less permeable and keeps the body warm. When the body is in a sweat condition, it allows the water vapor to escape into the environment because its moisture permeability becomes very high with increasing body temperature. This releases heat from the apparel. Using a composite film of shape memory polymers as an interlining provides [44] apparel systems with variable tog values to protect against a variety of weather conditions.

7.6.4 Sportswear

Sportswear should provide protection from wind and weather, dissipate perspiration, and have excellent stretch and recovery properties. Shape memory polyurethane fibers respond to external stimuli in a predetermined manner and are useful in sportswear.

7.7 Challenges and opportunities

The purpose in smart textile design is to utilize intelligent materials. Intelligent properties may be integrated in the material either in molecular or fibre level in the textile structure. The study of shape memory polymer has begun only in the last few years, and remains largely unexplored, and there are only a few marketable products. However, researchers are constantly finding combinations of technologies to increase avenues for commercialization. In general, thermally stimulated shape memory polymers show very large strains. There are many shape memory polymers that have been reported in the literature. Although these polymers have been proposed for a number of uses, their textile applications have been limited, due to the reversible temperature for the shape memory effects to be triggered is higher than the body temperature. Further investigations on the improvement of the induced strain magnitude, the stability of the strain characteristics with respect to temperature change, mechanical strength and durability after repeated driving are required to produce practical and reliable materials. The shape memory mechanism, the relation between structure and effect, especially their application to textiles and garments still have potentiality to develop. There are many challenges and opportunities in such an endeavor. Here, material design is very important for textile applications, especially their transition temperature to be triggered, and tailoring of hard and soft segment, as these all affect the shape recovery temperature, hand feel, etc. Compared with other types of shape memory materials such as shape memory alloys, the literature for understanding of the properties of shape memory polymers is still very fragmented and restricted. Investigation into their detailed characteristics and their potential is still required. Considering these factors, we think future research into the following will be interesting and challenging for the textile technologist:

- developing new shapes of polymer for textile applications
- shaping recovery to be triggered about room temperature/body temperature
- studying the relationship between shape memory polymer structure, ingredients and properties in function and processing
- adequately understanding the complexity of phase transformation systems and processes
- developing smart textiles with shape memory functions using shape memory polymer
- establishing the methods to evaluate the properties and performance of shape memory polymer and smart textiles.

7.8 Acknowledgement

The authors would like to acknowledge John Wiley and Sons Ltd., Elsevier Ltd., Artech House Publishers, for giving permission to reproduce their copyright material.

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8

Development of shape memory alloy fabrics for composite structures

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8.1 Introduction

Some smart materials have particular inner functions that allow them to be at the same time sensor and/or actuator.[1] They are able to instantly modify the physical properties (shape, conductivity, colour …) in response to natural or artificial events (variation in temperature, electrical or magnetic fields, mechanical strains). To put it in a nutshell, the material 'reacts' to an external stimulus and 'adapts' its behaviour. In particular, actuators provide a mechanical force or change their aspect (deformation, change of colour or opacity) in order to prevent a modification of the environment or to generate an active response. Three main categories of smart material can be distinguished:

1. The piezoelectric materials: they generate an electrical tension when they are submitted to a strain or inversely an electrical tension can provide a strain. The range and the frequency of the signal are directly correlated to the mechanical buckling.
2. The magnetostrictive or electrostrictive materials: under a magnetic (or respectively electrical) field, they can change their shape.
3. The shape memory alloy (SMA) materials: during the variation of temperature, they modify their crystal lattice structure to reach one of the metallic phases, martensitic, austenitic or a blend of martensitic and austenitic.

This chapter deals with the last category of smart materials, the shape memory alloy. A complete and brief description of their different properties helps us to well understand their amazing capacities. Then, a review of the different kinds of application is also given with respect to the presented properties. This will be followed by focusing on the different applications in the textile field, especially the interesting damping capacity of SMA fabrics for ballistic applications. Different future trends and ideas for using SMAs in textile structures will conclude the chapter.

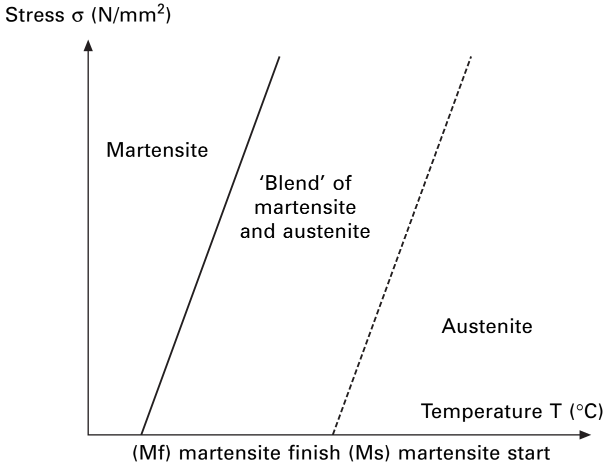
8.2 Definition and description of shape memory alloys

The shape memory effect was discovered in 1932 by Chang and Read on a gold-cadmium alloy. The same effect was also observed in 1938 on a zinc-copper alloy, lastly in 1963 on a nickel-titanium alloy. Afterwards, the first industrial applications were in the aeronautic field, for instance, a coupling system on F-14 aircraft in 1967. Since then these materials have found different applications in various industrial fields such as medical and biocompatibility, automotive, aeronautic and apparel.

Shape memory alloys have different mechanical behaviour from the usual materials. These are characterised by a specific state diagram of stress–temperature (see Fig. 8.1). As regards the temperature or the stress values, the material phase will be located in different areas as martensite, austenite or a blend of martensite and austenite. A complete and normalised definition of a shape memory alloy can be obtained in the French norm NF A51-080 (April 1991).[2]

In the same way as the martensitic changes in steels, the phase of 100% austenite in the material is obtained at high temperature and the phase of 100% martensite comes from the austenitic phase by cooling. The martensitic change presents four main characteristics:

1. the global motion of atoms occurs over very low distances
2. the transformation process occurs twice
   - first, change of the initial molecular structure to another
   - second, deformation of the crystal lattice



8.1 From austenite to martensite phases.

3. the martensitic transformation is quasi-instantly (higher than the speed of sound)
4. the volume variation is very low, but a shearing of the structure appears in a determined direction.

During cooling, the buckling of the crystal lattice is homogeneous. It occurs by sliding and then a rotation. A martensitic crystal lattice is obtained at low temperature. If the decrease in temperature has been achieved without stress, different kinds of martensite are obtained. The final buckling depends on the number of these different obtained martensites. It can vary from 3 to 8% for a polycrystal to 10% for a monocrystal.

8.3 Interesting properties of shape memory alloys

According to the different compositions of shape memory alloys, five main effects can be, most of the time, observed:[3]

1. Superelasticity; the alloy is able to buckle in a reversible process under stress.
2. Single memory effect; the alloy is able, after mechanical buckling, to recover its initial shape under a thermal process.
3. Double memory effect; the alloy is able, after a 'training' process, to keep two different shapes at two different temperatures.
4. 'Rubbery' effect; the alloy subjected to a stress retains, after the stress is removed, a residual buckling. If the material is repeatedly subjected to stress the residual buckling will increase.
5. Damping effect; the alloy is able to absorb shocks or to reduce mechanical vibrations.

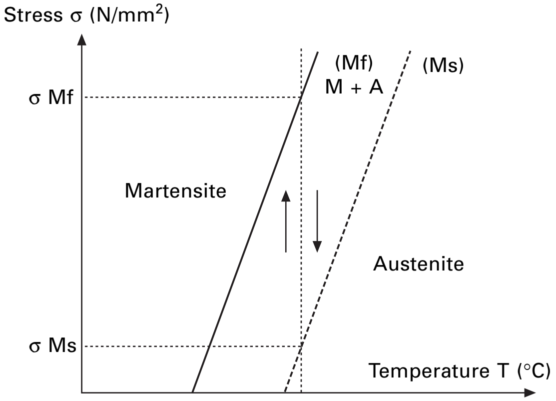
A complete and well referenced review of these different properties has been done by Wei *et al.*[4]

8.3.1 The superelasticity effect

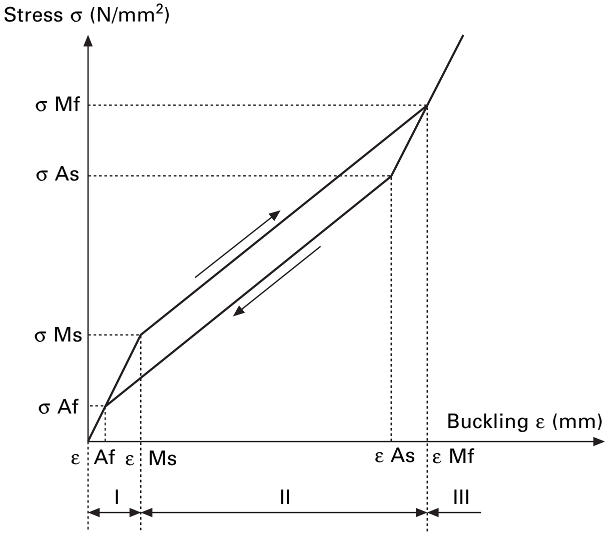
The shape memory alloys having this characteristic may be subjected to a more extreme buckling than a conventional alloy such as steel. The process of superelasticity can be explained as follows. A stress is applied on the alloy as shown in Fig. 8.2. At a constant temperature T and greater than the temperature of martensite start (Ms), the stress values begin from σMs (martensite start stress) to σMf (martensite final stress).

As it takes the strain, three areas can be distinguished along the Y axis (stress applied on the material) as shown in Fig. 8.3:

1. from the origin to σMs: elasticity of the austenite



8.2 The modification steps from austenite to martensite phases.



8.3 Tensile strength curve of a monocrystal shape memory alloy during change under stress at constant temperature.

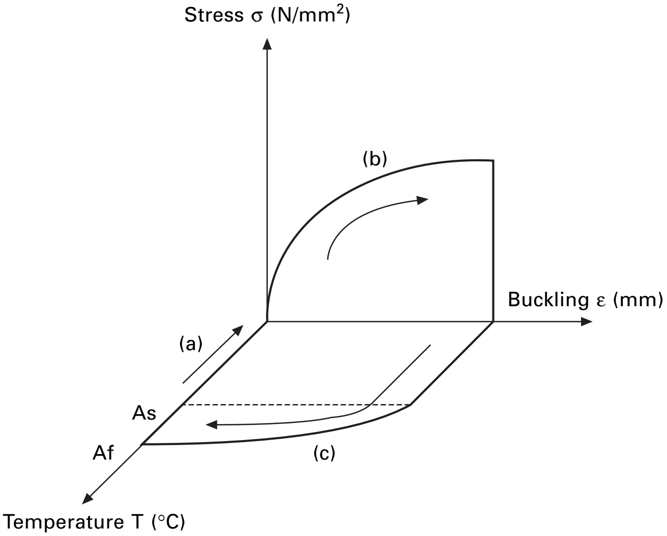
2. from σMs to σMf: buckling due to the martensitic transformation
3. from σMf: elasticity of the martensite.

It can be also noticed that when the strain is removed, the profile of the curve is similar to the one when the strain is applied but shifted by hysteresis. This is due to the fact that stresses σAs and σAf, respectively at the beginning and the end of the inverse transformation, are different from the stresses σMs and σMf, respectively at the beginning and end of the direct transformation.

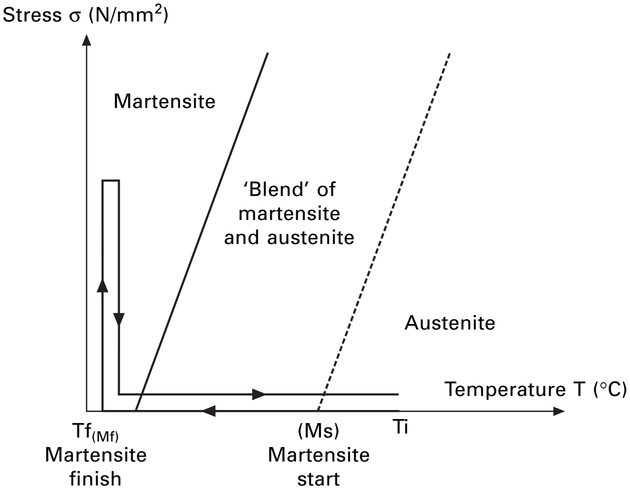
8.3.2 The single memory effect

This effect is observed when the alloy is submitted to a thermo-mechanical process corresponding to the following sequences (a) + (b) + (c) as shown in Fig. 8.4.

The single memory effect shown in Fig. 8.5 can be described as:



8.4 Thermo-mechanical process and single memory effect.



8.5 Sequences of the thermo-mechanical process allowing the single memory effect.

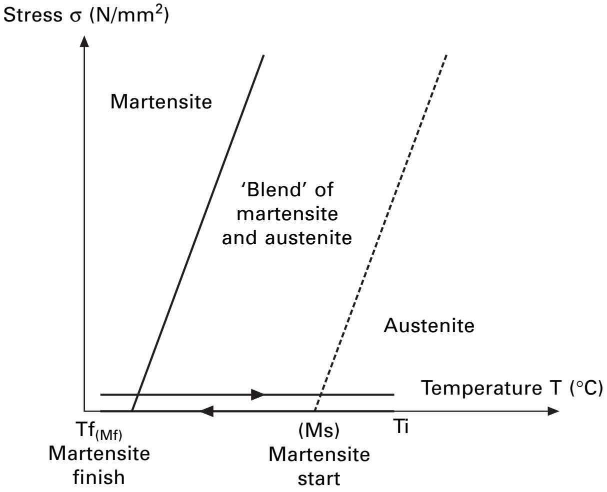
- Sequence (a): a cooling, without stress, from a Ti temperature greater than Ms to a Tf temperature less than Mf occurs. In this sequence, martensite is created in spite of the buckling of the material being null.
- Sequence (b): a stress is applied intermittently at a constant temperature, there is no phase change but a re-arrangement of the different kinds of martensite occurs during cooling.
- Sequence (c): heating is done up to a Ti temperature under a null stress. The alloy recovers its initial shape.

8.3.3 The double memory effect

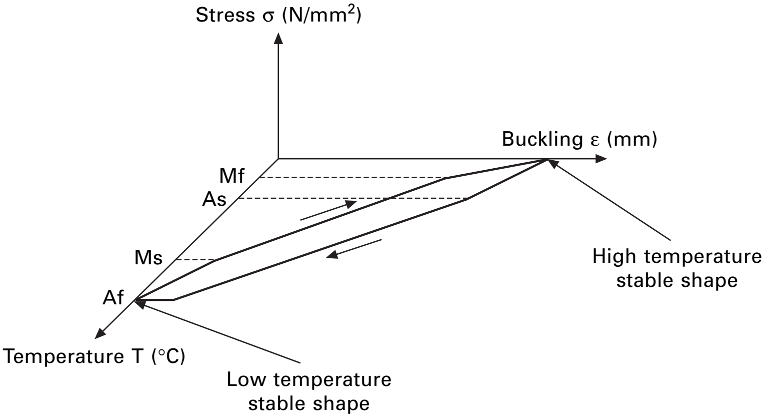
In the double memory effect, shape modification occurs at two different temperatures, high for the austenite and low for the martensite. The obtained shapes are stable and are obtained after a 'training' period, without any stress, as shown in Fig. 8.6. A transformation buckling εM is observed during cooling as shown in Fig. 8.7. The double memory effect can be qualified as a 'super-thermal' effect in which the applied stresses are recovered by internal stresses coming from the 'training' process.

8.3.4 The 'rubbery' effect

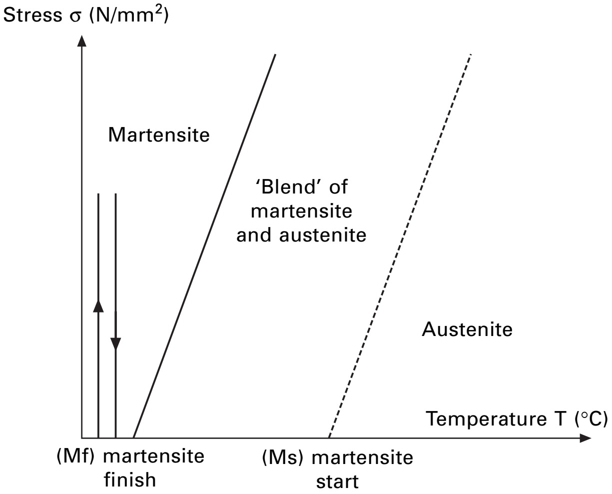
This behaviour is linked to an internal mechanism at the martensite phase (see Fig. 8.8); it seems to be partially reversible. For a given stress (see Fig. 8.9), the (ε) reverse buckling obtained is obviously greater than the (εe)



8.6 Thermal changes to obtain the double memory effect.



8.7 Double memory effect, without any external stress.

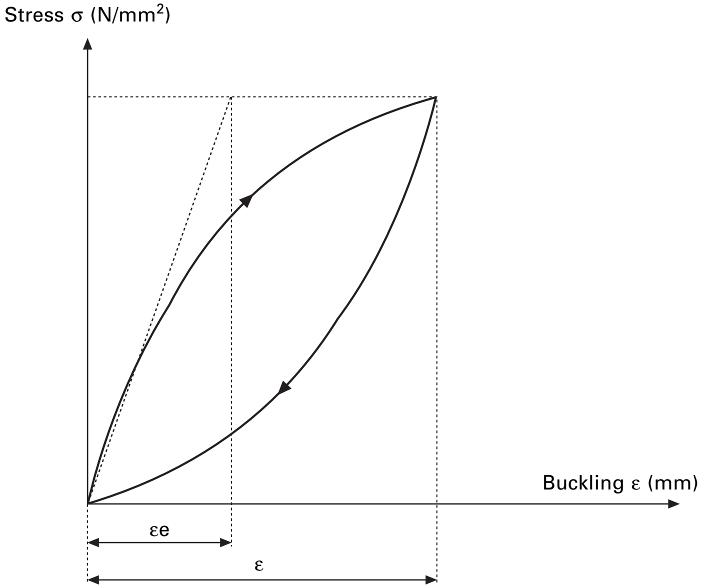


8.8 The 'rubbery' effect and the intermittent strain mechanical process.

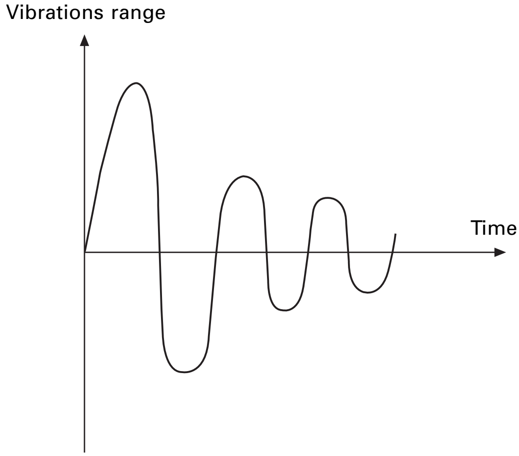
usual elastic buckling. Thus, the modulus is much less than the elastic modulus which conducts to a 'rubbery' effect.

8.3.5 The damping effect

This effect is mainly linked to the transformation phase at the solid state for which an initial austenite phase gives birth to a martensite phase, in a reversible manner from a crystallographic point of view. This effect is also called internal friction and can be observed, for instance, during free mechanical



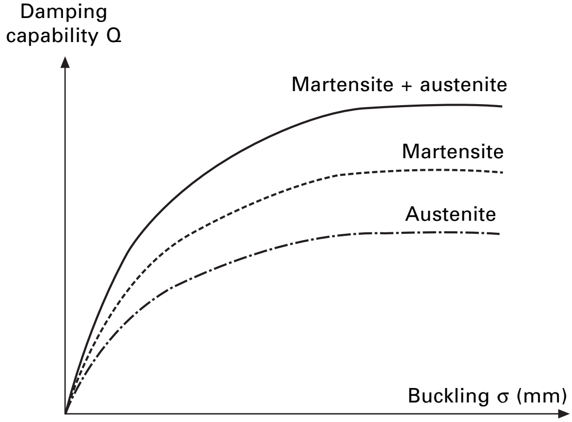
8.9 The 'rubbery' effect and the specific resulting buckling.



8.10 Decreasing of a vibration range due to internal friction of the material.

vibrations. A decreasing of the vibrations range with respect to the time occurs (see Fig. 8.10).

This friction is often characterised by a quality index Q also called the damping capability. According to the material phase and its buckling, three main areas can be observed (see Fig. 8.11) for which the shape memory alloy had different inner friction values:



8.11 Variation of the inner friction with respect to the three main phases of SMA.

1. In the austenite phase, the inner friction is low.
2. In the martensite phase, the inner friction is associated with a reversible motion of the different martensite phases.
3. Friction is highest in the transition zone of the austenite and martensite phases.

Although many alloys had some shape memory properties and damping capacity, only two families are mainly used for the development of SMA, the nickel-titanium and the copper base alloys. These two families have been highlighted due to their mechanical, thermal and electrical properties, their shape making ability, their way of making and their cost.

8.4 Different kinds of alloys

8.4.1 Nickel-titanium base alloy

The nickel-titanium alloy, commonly named as Nitinol, is the most studied and used in spite of its relatively high cost. Good characteristics such as the single memory and the superelastic effects are mentioned in Table 8.1. It can be made in different diameters as a wire (from 0.1 to 2.5 mm), but we have to bear in mind that the cost of the yarn is increasing exponentially with respect to the diameter reduction. In addition, Nitinol has good corrosion index properties, good fatigue performance and good compatibility with the human body.

To improve some properties of the nickel-titanium base alloy, small quantities of other elements could be added as mentioned in Table 8.2; copper (Cu) and iron (Fe) reduce hysteresis and nobium (Nb) increases the As temperature.

Table 8.1 Properties of the main different SMAs

Properties	Unit	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni	Cu-Al-Be
Composition		Nickel titanium	Copper zinc aluminium	Copper aluminium nickel	Copper aluminium beryllium
Melting point	°C	1260–1310	950–1020	1000–1050	970–990
Density	Kg/m3	6400–6500	7800–8000	7100–7200	7300
Young's modulus	Gpa	95	70–100	80–100	90
Tensile strength (in martensite domain)	Mpa	800–1000	800–900	1000	900–1000
Breaking strength elongation	%	30–50	15	8–10	15
Fatigue limit in austenite domain	Mpa	350	270	350	–
Transformation range	°C	–100 to 100	–100 to 100	–100 to 170	–200 to 150
Hysteresis (As–Mf)	°C	20–40	10–20	20–25	20–25
Spread (Af–As)	°C	30	10–20	20–30	15–20
Maximum buckling:					
Single memory effect		8	3–5	3–6	3–5
Double memory effect	%	5	2	3	2
Maximum temperature of use (1 hour)	°C	400	160	300	400
Maximum super elastic buckling					
Poly-crystal	%	4	2	2	3
Mono-crystal		10	10	10	10
Shock damping capacity (SDC)	%	15	30	10	–
Corrosion resistance		Excellent	Medium	Good	Medium
Bio-compatibility		Good	Bad	Bad	Bad

Table 8.2 Impact of an added element in nickel–titanium base alloy on different properties

	Hysteresis (°C)	Buckling (%)
Ni–Ti	20–40	6–8
Ni–Ti–Fe	2–3	1
Ni–Ti–Cu	10–15	4–5
Ni–Ti–Nb	60–100	6–8

8.4.2 Copper base alloy

As mentioned in Table 8.2, copper base alloys had less hysteresis than the nickel-titanium base alloys. Depending on their composition, wire diameters are also available from 0.1 mm to 2 mm. These different alloys are:

- Cu–Zn–Al is quite easy to produce at a moderate price but at a high temperature, its use is reduced due to a stabilisation of the martensite which increases the As temperature.
- Cu–Al–Ni, is difficult to produce but is not easily affected by stabilisation and ageing. This alloy has excellent properties in a wide range of temperatures (from 50 to 180 °C).
- Cu–Al–Be, has great thermal stability. The tiny quantity of beryllium allows the alloy to adjust its transformation temperatures from –200 to + 150 °C.

8.5 Different kinds of applications of shape memory alloys

The number of applications using SMAs is increasing as regards their specific properties, but limited to specific fields.[5] Principally, the limits of its use are governed by the cost of these materials and also by their low resistance, during their lifetime, to fatigue and ageing. At present, shape memory alloys can be found in the following.[6]

8.5.1 Bio-medical

Due to the bio-compatibility of nickel–titanium base alloys, many applications have occurred in the medical field. The following applications show the typical uses of SMA properties

- Medical staples are used inside the body. The main property required is the single memory effect. At the inner body temperature, the shape of the staple ensures the correct links which helps to fasten the fractured bones.[7]

- A 'stent' looks like a sort of braid which reverts to a wider diameter at body temperature. The 'stent' is inserted in arteries to regulate blood pressure. The property used is the single memory effect.[5]
- Another successful medical application is nitinol's use as a guide for catheters through blood vessels.[8] The main property involved is the superelastic effect.
- When used as a blood-clot filter, nickel–titanium wire is shaped to anchor itself in a vein and catch passing blood clots. Cooling the part allows it to be inserted into the vein and body heat is enough to transform it to its functional shape. The main property required is the single memory effect.[9]
- Orthodontic wires reduce the need to retighten and adjust the wire. These wires also accelerate tooth motion as they revert to their original shapes. The main property involved is the superelastic effect.[10]
- Nitinol needle wire localisers are used to locate and mark breast tumours so that subsequent surgery can be more exact and less invasive. The main property involved is the superelastic effect.[8]

8.5.2 Aeronautic and aerospace

Mainly due to their capacity to transform a thermal process into a mechanical process without any added parts, SMAs had been identified, in some cases, as the best solution in aeronautic and aerospace applications. The following listed existing applications are good examples.

- Nitinol couplers have been used in F-14 fighter planes since the late 1960s. These couplers join hydraulic lines tightly and easily.[11] The real success of these couplers lies in the fact that the shape memory effect was the unique solution. Tighter connections and more efficient installations result from the use of shape memory alloys.[12]
- Cryofit hydraulic couplings are manufactured as cylindrical sleeves slightly smaller than the tubing they are to join. Their diameters are then expanded while martensitic, and when warmed to austenite, their diameters shrink and hold the tube ends. The tubes prevent the coupling from recovering its manufactured shape, and the stresses created as it attempts to do so create an extremely strong joint.[13]
- In the Betalloy coupling, the shape memory cylinder shrinks on heating and acts as a driver to squeeze a thin liner onto the tubes being joined.[14]
- For satellite solar panels, the shape memory alloy actuator, using the single memory effect, opens the solar panels by heating.[15]

8.5.3 Automotive

Future applications are envisioned to include engines in cars and aeroplanes and electrical generators utilising the mechanical energy resulting from shape transformations. Nitinol, with its shape memory property, is also envisioned for use as car frames.[7] Other possible automotive applications using SMA springs include engine cooling, carburettor and engine lubrication controls, and the control of radiator blinds.[16]

8.5.4 Apparel and spectacles

- Brassieres using SMA bones are more comfortable using the super elastic effect. Moreover, bones are not bent in washing machines. These bras, which are engineered to be both comfortable and durable, are already extremely successful in Japan. The superelastic effect is mainly used in this application.[17]
- Spectacle frames using superelastic SMAs, are much more resistant to breaking. Nitinol eyeglass frames can be bent totally out of shape and return to their parent shape upon warming.[9]

8.5.5 Miscellaneous

Other miscellaneous applications of shape memory alloys include use in household appliances, in structures, in robotics and in security devices as listed below.

- A deep fryer utilises thermal sensitivity by lowering the basket into the oil at the correct temperature.[18]
- Nitinol actuators used in engine mounts and suspensions can also control vibration. These actuators are helpful in preventing the destruction of buildings and bridges.[19]
- A fire-sprinkler with an SMA spring reacts to a given temperature and actuates the sprinkler. The main advantage of nitinol-based fire sprinklers is the decrease in response time.[20]
- Anti-scalding SMA valves can be used in taps and shower heads. At a certain temperature, the device automatically shuts off the water flow.[21]

8.5.6 Use of SMA in ballistics

Since 2000, a GEMTEX laboratory team has been working on SMA fabrics, especially with nitinol wires, and a weaving technique has been developed[22] taking into account the same ideas as in the Japenese patent JP8209488 in 1996.[23] Special measures during the warping, drawing-in and weaving processes have to be taken in order to keep the material in an austenite phase. Thus, thanks to the fabric comprised of 100% nitinol SMA, as well as in the warp and weft directions, different properties have been shown with respect to damping capability[24] and the superelastic effect.[25] It follows from this that several experiments have to be conducted with SMA fabrics coupled with polyparaphenylene terephthalamide (PPTA) and high tenacity polyethylene (PE) fabrics to make a composite structure improving the high-velocity impact resistance.

First let us look at the different patents and publications dealing with composite structures and SMA damping properties required for ballistic application.[26] In one patent a plain warp-weft weave structure is used for high-tenacity yarns.[27] This weave diagram does not use the unidirectional yarns structure commonly used in the composite material. It aims to keep the main characteristics of the yarn in the woven structure but is easier to manipulate. Specific weave diagrams can be used in the backing structure to make high-performance yarns as functional as possible. In a second patent, an armour material for protection against ballistic, flame and blast attack is presented, having the form of a wire mesh structure where parallel weft rods of hard metal such as tungsten, titanium or austenitic steel are linked by flattened helix wires of a yielding material such as mild steel.[28] This knitted structure permits some elasticity which can be convenient for the behaviour of the material during the impact. The blend of different types of metallic yarns alternately in the weft direction allows exploitation of the best property of each wire. Thus, different types of fabrics composed of different yarns can also be used in ballistic applications.

Particular attention must be given to tough materials such as S-glass, aramids, and high-performance polyethylene which behave differently at higher strain rates.[29] In another patent dealing with methods of protecting structures from impact, the components are interposed between the point of impact and a structure to be protected.[30] They comprise an SMA exhibiting pseudoelastic behaviour, and having a high strain to failure ratio. The patent includes, experimental results on damping behaviour of a beam composed of shape memory wires under mechanical stress.[31] It is observed that the damping increases significantly when the shape memory wires are stressed such that they lie within the pseudoelastic hysteresis loop. These results demonstrate that pseudoelasticity of shape memory wires can be used to augment passive damping significantly in structural systems. This indicates that the SMA yarns to be used in our ballistics application have to be in a transition phase depending on the stress and the temperature. The superelastic SMAs are shown to be effective at low velocities and may also be in high ballistic velocity applications.[32]

A previous study was conducted by Kiesling and it was demonstrated that an increase of 41% of the energy absorption can be obtained with only 6% of SMA inserted in volume.[33] Thus, an adjusted proportion of SMA fabrics will be used in our ballistic application with respect to the total volume and weight. Recently, in the thesis work of Roger Ellis,[34] just after Paine and Kiesling,[35] the concept of using high-strain SMA and ECPE hybrid components to improve the ballistic impact resistance of graphite composites has been studied. The following obtained results have to be highlighted:

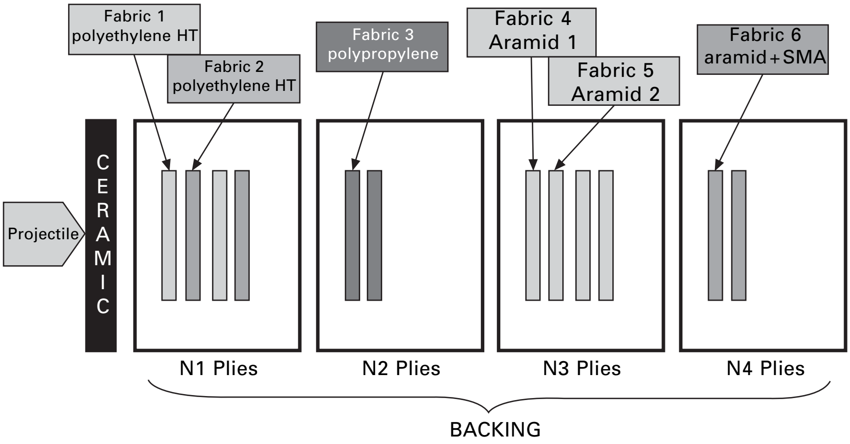
- A relative improvement of 99% of the energy absorption is observed when the Spectra^{TM} yarns are located at the back of the composite with an increase of only 12% of the total weight.
- Other and pure SMA fabrics must be tested by varying the yarns' diameters and the alloy compositions.
- At least, the recommended new structure to test tends to be knited rather than woven.

Finally, by taking into account all these previous results and recommendations, different backings have been realised made of pure aramid and blend of aramid and SMA fabrics corresponding to the NIJ Norm standard level 3 and 4.[36] At level 3, the armour protects against 7.62 mm full metal jacket bullets (US military designation M80), with nominal masses of 9.7 g impacting at a velocity of 838 m per second or less. Projectiles are fired six times at different locations. All the armours have been manufactured by MS Composite Company, during a final-year student project of six months. At the level 3, all the armours passed the ballistic tests. The mean resulted deformation after the impact for all these tests was very low. At the level 4, the armour protects against 30 calibre armour-piercing bullets (US military designation APM2), with nominal masses of 10.8 g impacting at a velocity of 868 m per second or less. Only one of five armours tested was failed at the level 4, mainly due to an excessive velocity of the projectile (measured at 890 m/s instead of 868 m/s). Faced with these promising results, we are engaged in a new campaign to develop new armour including a new kind of high-performance yarn. As a matter of fact, assuming a certain number of hypotheses and considering elementary computations on the buckling model of fabrics to impact, a new solution is proposed and will soon be tested. The new backing will integrate different fabrics with different type of yarns where each of them is used for its main property during impact. Its main composition is presented in Fig. 8.12.

The main properties of the four main blocks of the backing structure are detailed in Table 8.3. Thanks to a our previous tests and considering all the new recommendations, this new backing will succeed at different tests and especially reduce the blunt trauma.

8.6 Conclusion

The shape memory alloys have some different interesting properties than the other usual material such as steel. Various and numerous application fields of SMA demonstrate their advantages as regards these specific properties. In the ballistics domain, different ways put to the fore the main interest to make



8.12 Description of future backing structures under test.

Table 8.3 Functions of different fabrics inside the backing

N1 plies	N2 plies	N3 plies	N4 plies
Fabrics 1 and 2 made of PEHT yarns (Dyneema™) with respectively a higher linear capacity for fabric 1 than fabric 2. Each of these fabrics has a specific weave diagram in order to be well coupled.	Fabric 3 made of polypropylene high linear density yarns.	Fabric 4 and 5 made of high tenacity aramid (Technora™) with respectively a higher linear density for fabric 4 than fabric 5. Each of these fabrics has a specific weave diagram in order to be well coupled.	Fabric 6 made of SMA and aramid yarns
Awaiting function	Awaiting function	Awaiting function	Awaiting function
Decreasing of shearing stress and absorption of the main part of energy during projectile penetration.	Absorption of the calorific energy by melting	Decreasing of shearing stress.	In the transition zone of the SMA, damping capacity at impact.

a blend of different yarns inside the composite structure to take the benefit of each of their thermomechanical properties. Different tests have allowed validating a certain number of hypotheses as regards the yarns' behaviour at high-velocity impacts and specifically the SMA wires. The obtained results are sufficient but can be improved by varying a certain number of parameters to aim at a final composite structure solution optimising all criteria including the total cost and weight.

8.7 Future trends

The immediate future aims are the achievement of a new series of tests using our new backing structures to validate levels 3 and 4 of the NIJ norm as regards high-velocity impact. The mid-term future aims are linked to the results of the previous immediate ones. However, two different ways can be explored:

- improvement of the fabric process using SMA wires, especially the warping and weaving operations
- optimisation of the 'training' process of SMA, especially for fabrics structure.

At last, long-term future efforts could be shared by a large community and deal with the knowledge of the fabric's behaviour made from high-performance yarns with respect to different thermomechanical tests (tensile, compression, shear, bend, fatigue and age strengths) at different velocities (low, medium and high speeds) and under different environments (low and high temperatures). This global knowledge will help to validate mathematical models of behaviour of the textile structure.

8.8 Internet links

SMA Providers

Memometal technologies, Bruz, France.
http://www.memometal.com/FR/Default.htm
Nimesis, Metz, France
http://www.nimesis.com/
NitiFrance, Lury sur Arnon, France.
http://www.nitifrance.com/fr/
Memry Corp. – Bethel, CT
http://www.memry.com/
MicroGroup, Inc. – Medway, MA
http://www.microgroup.com
Electropolishing Systems, Inc. – Plymouth, MA
http://www.electropolishingsystems.com/
New England Precision Grinding – Holliston, MA – Contact
http://www.nepg1.com/

SMA applications

http://www.nimesis.com/francais/technique/amf/applications.htm
http://aml.seas.ucla.edu/research/areas/shape-memory-alloys/index.htm

SMA properties

http://www.nimesis.com/francais/technique/amf/amf.htm
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9

Study of shape memory polymer films for breathable textiles

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9.1 Introduction

Discussion of water vapor transfer will by nature focus on the ability of breathable textiles to reduce both heat stress and the uncomfortable sensation of wetness [1–2] whilst maintaining protection from wind and rain in comparison to totally impermeable fabrics [3]. In order to provide wearing comfort to the wearer, the garment should have a high capacity of water vapor transmission so that perspiration can evaporate and be transmitted from the body surface to the environment. Earlier fabrics coated/laminated with rubber or synthetic material, such as PVC, or acrylate were used as weatherproof clothing. These materials were watertight, however, their water vapor transmission was very low [4].

Today's modern technologies offer various possibilities for making waterproof and breathable textiles [5]. A well-known method to produce waterproof breathable textiles is to coat/laminate breathable nonporous films or laminate microporous films on a suitable base fabric's surface. Microporous film laminates 'breathe' due to their permanent, air-permeable pore structure. The basic principle consists of large numbers of micropores sufficiently large to allow the penetration of molecules of perspiration, but small enough to prevent water droplets going through the fabric [6]. Water vapor can easily escape from the body surface to the environment and prevent water droplet penetration. Because the diameter of a water vapor molecule is about 0.35 nm, while the diameter of a water droplet at standard pressure is bigger than 1 μm [7]. However, with the use of a porous film, deformation of films causes breaking or increases the size of pores that cause the delamination of coatings from the fabric surface and the water resistance becomes too poor. From the wearing point of view [8] the high water vapor permeability required for physiological comfort is important. Such moisture permeability cannot be obtained with a general nonporous polymer film. As the coated and laminated fabrics is composed of a thin layer of film and fabrics, so the film permeability plays an important role in order to make successful breathable textiles. In this chapter, we review the breathable textiles, followed by a study on microstructure and mass transfer properties of nonporous shape memory polyurethane films for breathable textiles described.

9.2 Breathability and clothing comfort

The movement of water vapor through a textile is an important factor in garment comfort. The human body attempts to maintain core body temperature around 98.6 °F. The balance between perspiration and heat production by the body and loss of the same is the comfort factor. The body would be in a state of comfort when the body temperature is about 35 °C and there is no moisture on the skin [9]. In order to maintain comfort, the primary functions of breathable textiles are:

1. to keep the wearer dry (from external water ingress and from internally generated condensation)
2. to provide protection against the cold
3. to protect against the wind chill factor, which is perhaps the bonus feature that the waterproof breathable textiles have due to their wind-resistant nature.

The total heat transfer through the clothing of the body to the environment, considering the thermal and evaporation resistance of the clothing, has been given by Woodcock [10]:

$$H = (T_s - T_a)/I + (P_s - P_a)/E \qquad 9.1$$

where H = total heat transfer, $T_s - T_a$ = temperature difference between skin and ambient, $P_s - P_a$ = water vapor pressure difference between skin and ambient, I = insulation of the clothing, and E = evaporation resistance of the clothing.

By incorporating thermal insulation products with waterproof, breathable textiles in the garment assembly, the effect of wind chill is greatly reduced. Through a combination of selected materials in the garment construction and suitable lining material, it is possible either to delay the formation of condensation by sweating and/or wick the condensed perspiration away during periods of activity in the inclement climates, thus increasing the wearer's comfort. It should be remembered that the body perspires to cool down during and after periods of strenuous activity and the fact that perspiring aids the return of body temperature to a comfortable balance. The perspiration rate of different activities are given in Table 9.1 [11].

Heat loss by evaporation is the only way to dissipate heat from the body when environmental temperature is greater than skin temperature. Liquid sweat is transformed into vapor at the skin surface, and it passes into the environment to cool. Evaporation of moisture from the skin surface is

Table 9.1 Approximate work and perspiration rates associated with various activities

Activity	Work rate (Watt)	Perspiration rate (g.day^{-1})	Limit of use			
Sleeping	60	2280				
Sitting	100	3800				
Gentle walking	200	7600	•			
Active walking	300	11,500	•			▶
with light pack	400	15,200		▲	■	▶
with heavy pack	500	19,000		▲	■	
in mountains	600–800	22,800–38,400		▲	■	
Very heavy work	1000–1200	38,000–45,600				

Note: • = coated; ▲ = hydrophilic membrane, ■ = microporous membrane; ▶ = woven cotton;   = woven microfibres (adapted with permission from Holmes D A, *J. Coated Fabrics*, **29** (4), (April 2000), 306 © Technomic Publishing Co. Inc. [11]).

tremendously effective in disposing of body heat. The loss of heat through perspiration and heat-flux through fabrics is very important. Part of this heat loss is by moisture evaporation. The greater the rate of moisture evaporation, the greater will be the comfort. Mass diffusion may also result from a temperature gradient in a system; this is called thermal diffusion. Similarly, a concentration gradient can give rise to a temperature gradient and a consequent heat transfer. In sum, cold weather clothing, besides insulating, should ideally have three main features, it should be water vapor permeable, windproof and waterproof. Two types of fabrics are in use for foul weather clothing. They are impermeable fabrics and breathable fabrics. An impermeable fabric is both wind and waterproof but not water vapor permeable. A breathable fabric, on the other hand, meets all the features of foul weather clothing and is water vapor permeable [10].

9.3 Breathable fabrics

Textiles with good breathing properties have become indispensable. They protect from rain, snow and wind but allow water vapor (perspiration) to penetrate. This guarantees a high level of comfort, especially when the article is worn during physical effort in sports and during work [12]. Many textile products are waterproof but only a few provide ‘breathability’. On the other hand, standard fabrics are ‘breathable’ but not waterproof. Some basic requirements of waterproof breathable textiles are summarized in Table 9.2.

9.3.1 Types of breathable fabrics

Breathable textiles can be categorized into four main types [10]:

Table 9.2 Basic requirements for waterproof breathable fabrics [13]

Waterproof breathable fabrics should, as indicated by the name, provide both waterproofness and breathability.
Windproofness
Abrasion resistance (wet and dry conditions)
Tear resistance
Strength of the coating/good adhesion of the membrane/film to the textile.
Easy care, wash resistance and washability
Lightness and packability (becoming increasingly popular for all outdoor activities)
Durability
Flexibility
Stretchability including stretch fabrics with thermal properties
Quietness
Handle, look, etc.
Other characteristics according to specific end uses: flame retardancy, chemical protection, high visibility, stain resistant and oil resistant

Note: besides these 'traditional' requirements the trend is clearly towards new functions and properties, such as 'clever fabrics', solar (UV) protection, sweat and moisture control (adapted with permission from Kramar L, *J. Coated Fabrics*, **28** (October), 1998, 107, © Technomic Publishing Co. Inc. [13]).

1. closely woven fabric with water-repellent treatment
2. microporous film laminates and coatings
3. hydrophilic film laminates and coatings
4. a combination of microporous coating with a hydrophilic top coat.

High-density-fabrics (HDF)

The fabrics can be woven with microfibers so densely that no interstices can be seen between the yarns. The microfibers are fibers that are less than 1 decitex per fiber. The fabrics made from microfibers are extremely soft and have a fine touch [5]. Water vapor permeability of such fabrics is high – a certain water resistance will be given by treatment with water-repellent agents such as flurocarbons and silicones. They provide for a higher watertightness as compared to the traditional textiles, but they do not give permanent protection in rain. Their water vapor permeability is excellent [4].

Examples are [5]:

1. Hoechst with its microfiber Trevira-Fineness (0.65 dpf) (polyester), which is used, for example, by Rotofil AG to weave their 'Climaguard'.
2. ICI with Tactel Micro/24 Carat (0.4 dpf) (polyamide) used, for example, by Finlayson in 'Microspirit'.
3. du Pont de Nemours fiber: 'Supplex' (0.9 dpf) (polyamide).

4. Burlington's: Versatech microfiber-based fabric.
5. Toray Ind. Inc. with 'Dyna-Bright' to weave their 'H_2Off'
6. Kuraray with 'Wramp' to weave 'Arcus'.

Microporous films, laminates and coatings

In the lamination technique a functional (water-resistant/breathable) barrier film is 'glued' to a suitable base fabric. Lamination of the film on a fabric uses special adhesives, sometimes even breathable ones. If non-breathable adhesives are used, care has to be taken not to cover the whole surface in the coating process. Microporous laminates/coatings 'breathe' due to their permanent, air-permeable pore structure. The basic principle consists of large number of micropores with a size sufficiently large to allow the penetration of molecules of perspiration, but small enough to prevent water droplets from going through the fabrics [13].

1. To render a film breathable, holes can be made in it: Teflon renders itself perfectly to this in a biaxial-stretching process, such as: Gore-Tex (W.L. Gore/USA) and Microtex (Nitto Elec. Ind./Japan).
2. Polyurethane/polyacrylate microporous film is also available, such as: Porelle film made by Porvair/GB in a coagulation process or Repel film (polyacrylate) made by Gelman Science/U.S.A. in a photopolymerization process.

Hydrophilic film laminates and coatings

The solid, or compact, structure of the product prevents penetration of water droplets whereas transmission of water vapor is provided by a molecular mechanism (absorption-diffusion-desorption) [13]. From the hydrophilic group containing polyurethane solution the solvent will be evaporated leaving a compact film behind [4]. Hydrophilic groups built into the polymer chains can absorb, diffuse, and desorb water vapor molecules through the film [14], examples are [5]:

1. Sympatex film (polyester), a product of Enka Glanzstoff (D)
2. Bion II film (polyurethane), a product of Toyo Cloth C°/J
3. Excepor-U (polyamioacid/PU), a product of Mitsubishi-Kasei.

A combination of microporous coatings with hydrophilic top coat

The combination of microporous and hydrophilic layers is also possible [13]. A microporous coating or film, for example, can be further coated with a hydrophilic layer in order to increase waterproofness, and to seal the surface pores, reducing the possibility of contamination of the microporous layer by dust particles, detergents, pesticides, etc. A hydrophilic finish on a microporous structure is used to upgrade the water-resistance of microporous coatings. Care has to be taken to select a hydrophilic finish that does not impart an unacceptable decrease in breathability. Ucecoat NPU2307 finish on top of Ucecoat 2000 (S) microporous coating is an example [5].

9.3.2 Merits of nonporous over porous films for breathable laminates

Waterproof breathable textiles could be made by coating or laminating microporous film on a suitable base fabric. The water droplet penetration is effected via micro-fine pores which are produced by a special process during the production of the film or during coating. While perspiration can easily escape from the body surface to the environment very quickly, small drops of rain or spray cannot penetrate this breathable system, despite its pore structure because the diameter of water vapor molecules is 0.35 nm and of water droplets about 1 μm [7].

Besides the famous PTFE membranes (Gore-Tex, Gore), where the pores are achieved during production by stretching the membranes, there are also microporous hydrophobic polyurethane membranes on the market. The pores of these membranes are also produced by a special coagulation process [12]. The advantages of microporous membranes are [13]:

1. Better breathability: hydrophilic coatings/lamination is influenced by the thickness of the coating/laminates and number of hydrophilic groups present in the film structure.
2. Better handling: hydrophilic coating has a stiffer handle.
3. Hydrophilic coating tends to wrinkle in wet conditions.

Despite better breathability, the microporous films have several disadvantages, such as:

1. Pore sealing of micropore of coating or laminates occurs during usage and affects breathability. The pore-sealing micropores can be contaminated by a number of agencies, including particulate and air-borne dirt, pesticide residues, insect repellents, sun tan lotions, salts (marine environment), skin exudates, and detergents and surfactants used for laundering or drycleaning. All of these contaminants have been suspected of lowering the breathability [15].
2. During the use of microporous film, deformation of film causes films to break or an increase in the size of pores so that water proofness becomes too poor for practical use. Numerous small degraded loose segments can easily mix with human sweat, becoming an ideal culture medium in which bacteria and mold can grow. If the latter happens, the fabric can

easily be affected by all kinds of microorganism (e.g. bacteria and mildew) and deteriorate the films, thus affecting the waterproofness as well as fabric appearance.

3. Microporous film has a poor tearing strength compared to the solid structure of a nonporous one.

Compared to the microporus films the advantages of nonporous breathable films are as follows:

1. The film-making procedure is simple and the production speed is higher.
2. Having a solid structure and no holes the nonporous films are less sensitive to possible degradation.

Table 9.3 shows some features of nonporous and microporous films for textile lamination.

Having solid structures, nonporous films possess several advantages compared to microporous films. Since a certain amount of water vapor permeability is required in order to give the wearer comfort, how to improve the permeability of nonporous membranes is really a challenge for polymer chemists. Permeability of nonporous membranes could be enhanced by introducing hydrophilic groups into the polymer backbone, as the permeability occurs through the nonporous films by molecular mechanism (sorption–diffusion–desorption). However, too many hydrophilic groups causes swelling and weight loss of film increases during washing due to increasing solubility, and waterproofness continues to decrease after each wash [13]. The option may be in the shape memory polymer (SMP) films, the large change of mechanical and thermomechanical properties occurs across the glass transition temperature (T_g) or soft segment crystal melting point temperature (T_{ms}) [17].

In addition to the mechanical properties of SMP, it was found that SMP also undergoes a large change in moisture permeability above and below the T_g/T_{ms}. Based on the T_g/T_{ms} set at room temperature, the SMP has low moisture permeability below the T_g/T_{ms} and during the glassy state, and has high moisture permeability above T_g/T_{ms}, and during the rubbery state. This

Table 9.3 Features of microporous and nonporous films [16]

Nonporous	Microporous
Windproof	Windproof (arguments)
Waterproof and liquid proof	Waterproof and liquid resistance
Selective permeability	Non-selective permeability
High water entry pressure	Low water entry pressure
Good tearing strength	Low tearing strength
High water vapor transmission	High water vapor transmission

(Adapted with permission from Johnson L., and Samms, J., *J. Coated Fabrics*, 27 (July), (1997), 48 © Technolmic Publishing Co. Inc [16]).

behavior can be used with SMP-laminated textiles that could provide thermal insulation at cold temperatures and high permeability at room temperature or above.

9.3.3 Designing breathable textiles with nonporous films

Technical discussion of waterproof breathable fabrics usually raises the highly contentious subject of water vapor transmission properties. In this context, breathability refers to the capacity of a fabric layer, garment or clothing assembly to transmit water vapor, emitted from the body as perspiration, to the outside atmosphere. A discussion on the mechanism of water vapor permeability is useful in understanding the principle of designing breathable fabrics. Mass transfer through porous film occurs through the permanent pore structure of porous film. But non-porous films are dense, pinhole-free polymer membranes. These polymer films are also usually hydrophilic and absorb water very quickly. This is an important property that produces a ‘wicking’ action that actively attracts water vapor molecules. Non-porous film allows the transmission of water vapor through a process called active diffusion. This is the same transport mechanism by which helium escapes from a toy balloon. The permeant dissolves on the surface of the film on the side of the highest concentration, and then diffuses across the film. When the vapor arrives at the opposite surface, the permeant desorbs and typically enters the surrounding airspace as gas or vapor. Water vapor transfer through a nonporous membrane occurs in molecular mechanism, i.e., sorption-diffusion-desorption. A discussion of the mechanism of water vapor transfer through nonporous films follows.

Since in nonporous films, there are no micropores mass transfer can result from different phenomena [18]. There is a mass transfer associated with convection in that mass is transported from one place to another in the flow system. This type of mass transfer occurs on a macroscopic level and is usually treated by the subject of fluid mechanics. There will be a mass transfer on a microscopic level as the result of diffusion from regions of high concentration to regions of low concentration due to the concentration gradient. Higher concentration means there are more molecules per unit volume. Mass diffusion may also result from a temperature gradient in a system; this is called thermal diffusion. Similarly, a concentration gradient can give rise to a temperature gradient and a consequent heat transfer. Permeation is a collective process of diffusion and sorption and hence, the permeability of mass molecules in polymer depends both on diffusion and solubility [18]. Chemical structure and film thickness are the main determinants of permeability in a nonporous membrane [19].

Structural factors influencing film permeability

Not only the polymer-penetrant interaction but also the primary structure of the polymer itself are very important for an understanding of film functions such as sorption, diffusivity, and permeability of small molecules [20]. The cohesive energy of polymer membranes is determined by such factors as chain flexibility (internal rotation of repeating unit), coulombic interaction, van der Waals interaction, hydrogen bonding, and so on. A high permeability coefficient is generally attained when each factor except flexibility is low and is not affected by the penetrant. Therefore the polymer, which contains a monomer unit with a high charge density, dipole moment, and capability for hydrogen bonding, will give a low permeability coefficient. Cipriano *et al.* stated that the permeant fluxes increase with the increasing value of the prepolymers molecular weight [21]. This means that longer molecular chains originate larger polymer network holes and therefore higher water vapor fluxes.

Film thickness influencing permeability

Fick's law governs the rate of transport of the permeant through the film under the existing concentration gradient. If the diffusion coefficient (D) is not a function of concentration, integration across the film thickness l is given by [18]:

$$J = D(c_1 - c_2)/l \tag{9.2}$$

Where c_1 and c_2 are the concentrations of permeant at the high and low pressure faces of the film surface, and l is the thickness of the membrane. A linear relationship between the concentration of water vapor in equilibrium with the film and actual concentration of water vapor dissolved in the film is assumed by Henry's law as given in eqn 9.3, which holds for many polymers:

$$c = Sp \tag{9.3}$$

Substituting, values of c_1 and c_2 from eqn 9.3, eqn 9.2 becomes:

$$J = DS(p_1 - p_2)/l \tag{9.4}$$

Where p_1 and p_2 are the external partial pressure of the vapor on the high and low pressure sides of the membrane respectively. (DS) is termed as the permeability (P). From eqn 9.4, it is clear that for ideal systems, the permeation rate of permeant is directly proportional to the pressure gradient and inversely proportional to membrane thickness.

9.4 Water vapor permeability (WVP) through shape memory polyurethane

9.4.1 Glass transition temperature as transition point for WVP [22]

Experimental

Shape memory polyurethane (SMP), MS-4510, with a solids content of 30%, was supplied by Mitsubishi Heavy Industries Ltd., Japan. N,N'-dimethyl formamide (DMF) was obtained from BDH laboratory, England. The solution of SMP was dissolved to form 15% by weight solution. The film was cast on a glass plate by doctor blade. Three casting temperatures were chosen; 70, 120 and 150 °C, and the resultant films were coded as SMP-70, SMP-120 and SMP-150, respectively. DSC measurements were carried out over the temperature range of –50 to 220 °C using a Perkin Elmer 7 Series DSC, purging with N_2 and chilled with liquid N_2, about 10 mg of sample scanned at a heating rate of 10 °C/min.

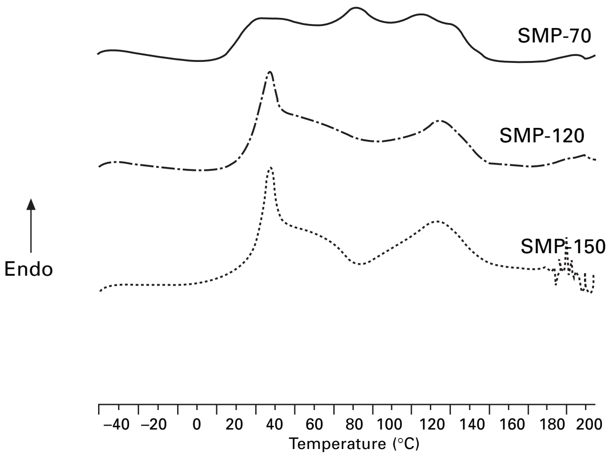
Dynamic mechanical properties were measured with a dynamic mechanical thermal analyzer (Rheometry Scientific DMTA MK 3). The samples (10 × 3 × 0.03 mm) were investigated in the temperature range from –50 to 120 °C, using the tensile mode at the heating rate of 5 °C min^{-1} and a frequency of 1 Hz under N_2 gas purging. A length to thickness ratio of samples is larger than 10 for neglecting the DMA's dependence on the Poisson ratio. The maximum peak of the tan (delta) curve is considered as glass transition temperature.

The shape memory effect was examined by bending mode [23]. The samples were deformed to an angle θ_i (~90°) at a bending temperature (T_b = 100 °C), well above T_g of the samples, and kept the bending time (t_b = 2 min). Then the deformed samples were quenched to 0 °C for about 1 min and then the external force released. The deformed samples were heated at a constant heating rate and recorded the data of the angle θ_f and the corresponding temperature. The recovery ratio was defined as $(\theta_i - \theta_f)/\theta_i \times 100\%$.

Water vapor permeability (WVP) was measured according to ASTM D1653-93. That is, an open cup containing distilled water was sealed with the cast film of SMP, and the assembly was placed in the test chamber with a controlled temperature (25 °C, 35 °C, 40 °C, 50 °C and 60 °C) and humidity (relative humidity (RH) 80%, 65%, 40%). The steady water vapor flow was measured by plotting the weight change of the cup containing the water against time.

Results and discussion

DSC curves and thermal data of shape memory polyurethane samples are shown in Fig. 9.1 and Table 9.4. The glass transition temperature of the soft



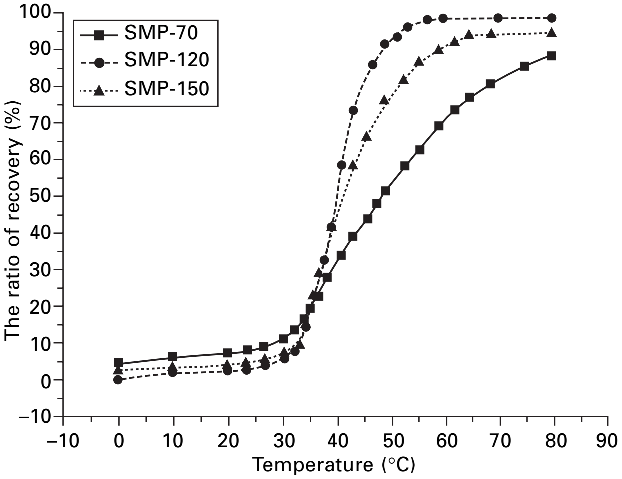
9.1 DSC thermogram of SMP (adapted with permission of ref. 22).

Table 9.4 Thermal data of DSC testing (Adopted with permission of ref. 22)

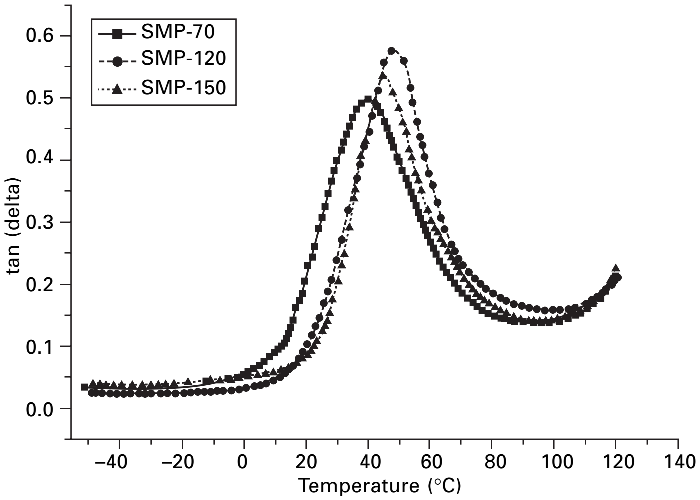
Samples	Tg, °C	ΔH_1, J/g	T_{mh}, °C	ΔH_2, J/g
SMP-70	31	–	125.8	7.9
SMP-120	39.2	16.8	136.3	27.5
SMP-150	41.5	20.9	133.3	51.2

segment (T_g) is 30–42 °C in DSC curves, and the stress relaxation peak (ΔH_1) appears at the glass transition domain both in SMP-120 and SMP-150 because the hard segment restricts the mobility of the soft segment due to the increased crystallinity of the hard segment. The second transition (T_{mh}) is an endotherm (ΔH_2) in the range of 135 °C, indicating the melting of hard segment crystals. These results showed that SMP-120 and SMP-150 are phase separated into an amorphous soft segment domain and a partially crystalline hard segment domain. However, the transition in SMP-70 is very weak and two small endothermic peaks appear at temperatures of about 90 and 125 °C due to the dissolution of the hard segment in the soft domain and the lower degree of segment separation. The DSC curves confirm that the film preparation at lower temperatures, such as sample SMP-70, are not favorable for crystallization of the hard segment and therefore segment separation.

The shape memory effect of SMP at different temperatures, is shown in Fig. 9.2. The recoverable ratio of the specimens was less than 10% at a low temperature range (0 to 30 °C). The SMP-120 recovered deformation rapidly when it was heated to a high temperature, and little residual deformation remained; the SMP-70 showed a wider temperature range for recovering and



9.2 Shape memory behavior of SMP films (adapted with permission of ref. 22).

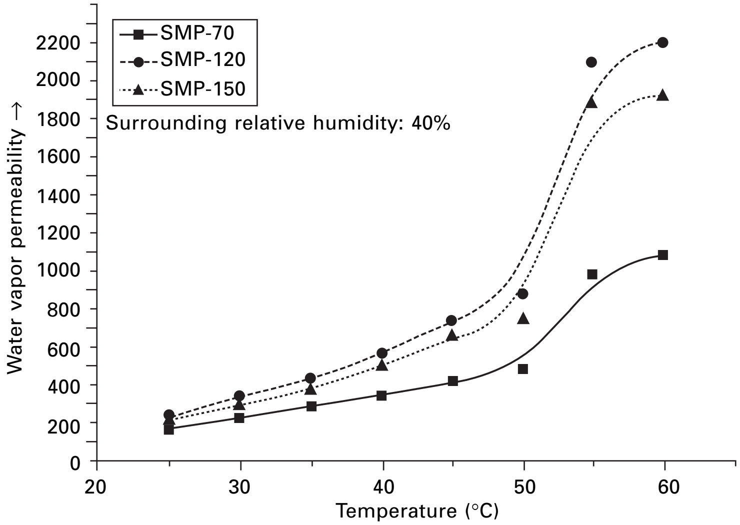


9.3 Loss tan (delta) of SMP films (adapted with permission of ref. 22).

a smaller recovering ratio than the others. These results demonstrated that the shape memory behavior of SMP is influenced by the morphology of the soft and hard segment phase domains [24]. Their recovering ratio is directly related to their storage modulus ratio, that is, the SMP films could show better shape memory behavior if their storage modulus ratio were high Fig. 9.3 and Table 9.5. Consequently, the SMP-120, with a high modulus ratio, shows better behavior of deformation recovery than the others. The crystallinity in the hard segment domain is good for keeping the deformation at a temperature

Table 9.5 DMTA data of SMP films (Adopted with permission of ref. 22)

Samples	Glass transition temperature (T_g)	Storage modulus ratio ($E'_{Tg-20°C}/E'_{Tg+20°C}$)
SMP-70	24	137.7
SMP-120	31	293.9
SMP-150	34	194.0



9.4 Water vapor permeability of SMP films (adapted with permission of ref. 22).

range lower than the T_g of the soft segment and recovery to the original shape with the heating process.

The water vapor permeabilities variations of shape memory polyurethane films at different temperatures are shown in Fig. 9.4. Water vapor permeability increases appreciably above the T_g of the soft segment in all samples. This shows that moderate crystallinity is more suitable for better water vapor permeability than low and very high crystallinity according to the thermal data of all samples (Table 9.4). We can explain this as follows: generally, the permeability of small molecules through the polymer membranes is enhanced when their diffusivity increases with increasing temperatures [25–26]. According to the concept of free volume in polymers, the glass transition occurs in the polymers when the fractional free volume (FFV, the ratio of the free volume and specific volume in polymers) reaches the standard value of $f_g = 0.025$. Above T_g, that is, in the rubbery state, FFV increases linearly with temperature:

$$FFV = F_g + (\alpha_1 - \alpha_2)(T - T_g) \qquad 9.5$$

where α_1 and α_2 are thermal expansion coefficients in the rubbery and glass states, respectively.

This increases the free volume in the polymer, and the micro-Brownian motion of the soft segment obviously increases to make the intermolecular gap large enough to allow water vapor molecules to be transmitted through the SMP film. That is, the diffusivity of water vapor molecules in the SMP film increases with increasing temperature. Therefore, large changes in moisture vapor permeability above and below the T_g of the soft segment are observed. However, the glassy state of the soft segment at low temperature plays the role of water vapor barrier, so it decreases the water vapor permeability and provides a waterproof barrier at low temperature.

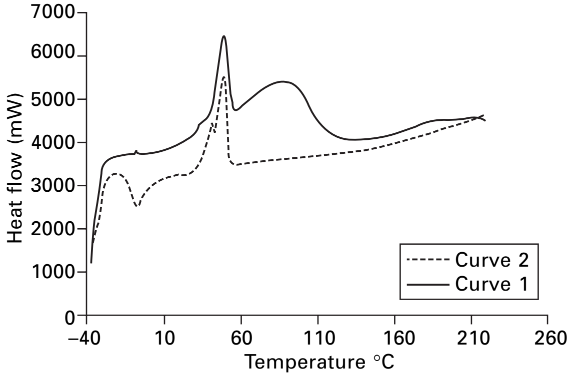
9.4.2 Soft segment crystal melting temperature as transition point for WVP [27]

Experimental

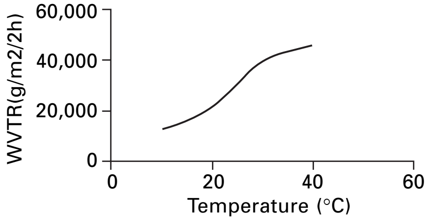
The shape memory polyurethane (SMPU) used for this study was obtained from Mitsubishi Heavy Industries. Differential scanning calorimetry (DSC) was carried out over a temperature range from –40 °C to 220 °C using a Perkin Elmer DSC7. The samples were scanned at a heating rate of 10 °C/min and sample weight was 9.6 mg. After the first scan, melted specimen was quenched to –40 °C at a cooling rate of 20 °C/min. The sample was again scanned at 10 °C/min. SMPU film was sealed over the open mouth of a test dish which contained water, and the assembly placed in a controlled atmosphere. After keeping at 10 °C, 20 °C, 30 °C, 40 °C for 24 hours, the dish was weighed and the rate of water vapour permeation through the film was determined.

Results and discussion

The DSC thermogram of SMPU is shown in Fig. 9.5. DSC curve 1 was obtained over a temperature range from –40 to 220 °C at a heating rate of 10 °C/min. It showed that the endothermic peak began from about 10 °C, and the highest point of the peak was at 50 °C, which was caused by crystal melting. DSC curve 2 was obtained over the same temperature range at the same heating rate as curve 1 after quenching to –40 °C. There was only one exothermic peak at –10°C and one endothermic peak at 50 °C, which was related to re-crystallization and crystal melting, respectively. This result could support the curve 1 findings. With the temperature rising further, we saw no distinct endothermic peak from curve 2, indicating that only soft segments formed crystal structure in the SMPU.



9.5 DSC curve of SMPU (adapted with permission of ref. 27).



9.6 Temperature-dependent water vapor permeability of SMPU films (adapted with permission of ref. 27).

Figure 9.6 shows the relationship between water vapor permeability of SMPU film and temperature. When the temperature rises from 10 to 40 °C, i.e., in the soft segment crystal melting range, WVP increases significantly. In theory, the phase transition of a polymer from the crystalline to the amorphous phase will result in an increased amorphous area, which will also lead to increased free volume. It is well known that for dense samples, water vapor transport proceeds by diffusion through the film by free volume theory, driven by vapor concentration difference [28]. When the experimental temperature reaches crystal melting point temperature, the relative amount of amorphous area increases, which leads to increased free volume, therefore the film can provide more paths for water vapor permeation, and thus the WVP increases significantly.

9.4.3 Soft segment crystal melting temperature as transition point at room temperature

Experimental

Polytetramethylene glycol (M_n = 2000 g mol^{-1}, PTMG 2000)-based temperature-sensitive shape memory polyurethanes (TSPU) were synthesized

Table 9.6 Composition of TSPU [29]

Sample code	Feed ($\times10^{-3}$ mol)				
	PTMG2000	PEG	MDI	1,4-BDO	PEG (wt %)
S_6	14.75	22.5 (PEG-200)	44	7.15	9.86
S_7	14.75	2.25 (PEG-2000)	37	20	9.98
S_8	14.75	1.33 (PEG-3400)	36.08	20	10.03
S_9	9	–	38	28.79	–

(Adapted with permission from Hu J. L., and Mondal, S., *Polym. Inter.*, in press, © 2005, John Wiley and Sons Ltd. [29]).

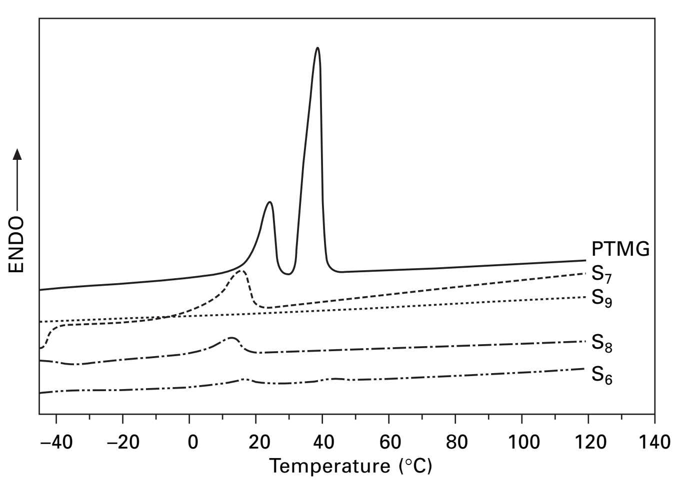
with three different block lengths of hydrophilic segment, polyethylene glycol (M_n = 200, 2000 and 3400 g mol^{-1}, PEG 200, PEG 2000 and PEG 3400), by a two step polymerization process [28]. The detailed compositions are given in Table 9.6.

Membranes were cast from diluted PU solution (concentration about 5% w/v) in N,N-dimethyl formamide (DMF) on Teflon coated steel plate. In order to obtain pinhole free membrane, solvent was evaporated slowly at 60 °C for 12 h and final residual solvents were removed under vacuum at 80 °C for another 12 h. Then the Teflon plates were removed from the vacuum oven and kept at room temperature for 2 h. After 2 h membranes were removed from the Teflon plate. The thickness of the membranes was 45–60 μm for mass transfer.

Perkin-Elmer DSC 7 was used to measure the heat of fusion (ΔH), T_m, etc. Each sample having a weight from 5 to 10 mg was scanned from –50 to 120 °C at a scanning rate of 10 °C min^{-1} under dry nitrogen purge. In order to find the role of PTMG in the PU, the DSC and WAXD testing for pure PTMG was carried out. The water vapor flux (WVF) was measured according to ASTM method E 96-80B. Round-mouth conical plastic cups with a diameter of 60 mm and a height of 90 mm were filled with deionized water. Membranes were placed over the top of the cups, securing perfect sealing between cup and membranes. The gap between the membranes and water surface was about 4 mm. The cups were placed in a constant temperature chamber at the desired temperature (12, 18, 25, 35 or 45 °C). During all WVF measurements air surrounding the membranes had a constant temperature and 70% relative humidity. An average of three different samples was used for each WVF measurement, which are expressed in the units g m^{-2} d^{-1}, where d is a day (24 h).

Results and discussions

DSC results are shown in Fig. 9.7 and Table 9.7. From Fig. 9.7, it can be seen that no endothermic peak was observed for the sample S_9 containing no



9.7 Heating thermogram of PTMG and related TSPU (adapted with permission from Hu J. L., and Mondal, S., *Polym. Inter.*, in press, © 2005, John Wiley and Sons Ltd. [29]).

Table 9.7 DSC data of TSPU [29]

Samples	ΔH_1^a	T_{ms1}^b	ΔH_2^a	T_{ms2}^b
S_6	0.66	15.50	0.32	42.83
S_7	28.37	15.67	–	–
S_8	22.52	12.83	–	–
S_9	–	–	–	–
PTMG	32.34	24.50	81.13	39.00

ΔH is heat of fusion, T_{ms} crystal melting temperature, T_g glass transition temperature, ^{a}data are in g J^{-1} or ^{b} are in °C (adapted with permission from Hu J. L., and Mondal, S., *Polym. Inter.*, in press, © 2005, John Wiley and Sons Ltd. [29]).

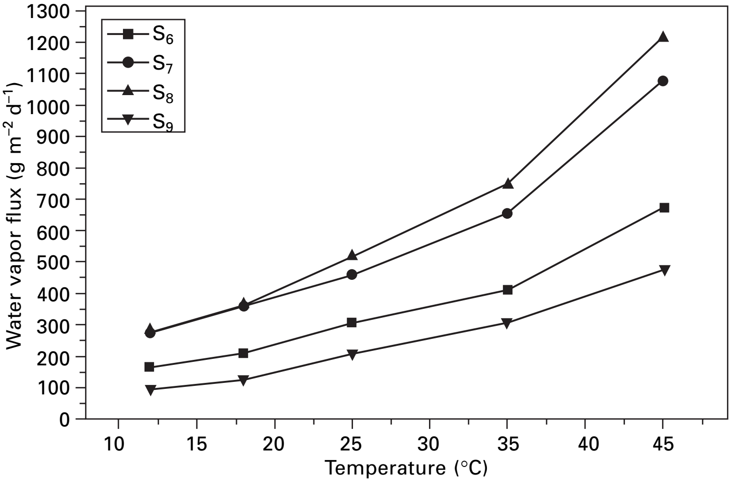
hydrophilic segments. That may be due to the flexible nature of the PTMG soft matrix, where hard segments act as a reinforcing filler and prevent the crystallization of the soft matrix. On the other hand, introducing the hydrophilic segment in the PU enhances the crystallization of the soft matrix, that may be due to the PEG segment increasing the mobility of the polymer molecule, which facilitates the crystallization process. With low molecular weight PEG-200, the actual percentage crystallinity is very low compared to the calculated percentage crystallinity from polyol weight fraction, and may be due to the plasticization effect of PEG-200, that would not make for favorable conditions for soft segment crystallization. The percentage crystallinity is highest with PEG-2000 as compared with PEG-200 and PEG-3400. This results from the fact that crystallization in polymers involves the steps of (primary) nucleation and relatively rapid spherulitic growth, followed by a slow, kinetically difficult improvement in crystal perfection [30]. The molecule must undergo a considerable degree of motion during crystallization. The motion may be optimum with PEG-2000, because this molecular weight is comparable with polyol (PTMG) molecular weight, 2000 g mol^{-1}, and enhanced intermolecular packing of small crystalline domains. The decreased percentage crystallinity with PEG-3400, may be due to chain entanglement, which hinders the crystallization process of the soft domain.

The water vapor flux (WVF) data are shown in Table 9.8 and Fig. 9.8. From Table 9.8 we can see that in all cases WVF increases with temperature, due to two reasons. First of all as the temperature increases the difference in the saturation vapor pressure of water in the cup and surroundings also increases, which would also increase permeability. The second reason is the

Table 9.8 Water vapor flux data of TSPU [29]

	WVF (g m^{-2} d^{-1})				
Sample	12 °C	18 °C	25 °C	35 °C	45 °C
S_6	170	210	310	410	680
S_7	276	359	460	660	1080
S_8	280	365	520	750	1220
S_9	96	124	210	310	480

(Adapted with permission from Hu J. L., and Mondal, S., *Polym. Inter.*, in press, © 2005, John Wiley and Sons Ltd. [29]).

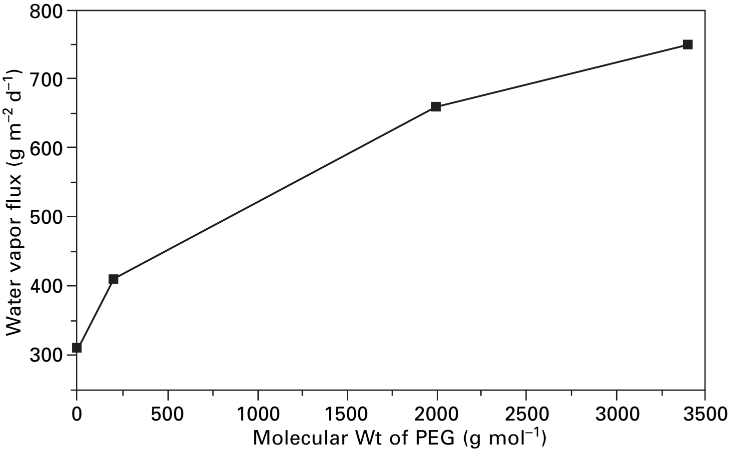


9.8 WVF results of TSPU at different experimental temperatures (adapted with permission from Hu J. L., and Mondal, S., *Polym. Inter.*, in press, © 2005, John Wiley and Sons Ltd. [29]).

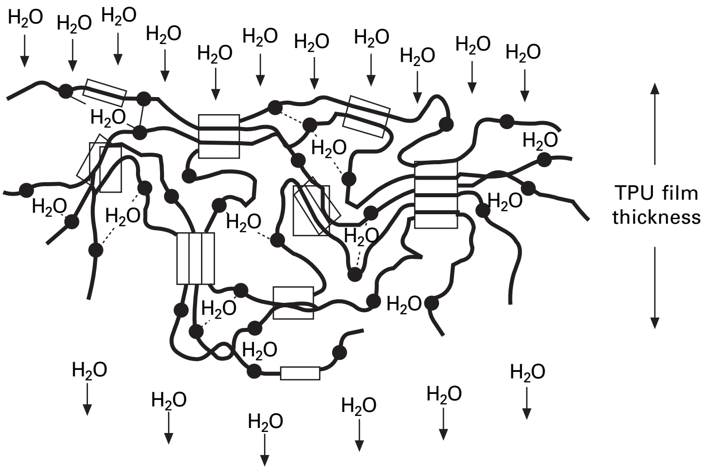
structural change with increasing temperature. In all cases first factor remains constant, so the differences of water vapor permeability at a particular temperature is due to the change in morphological structure.

The permeability of small molecules through the nonporous polymer membrane is enhanced when their solubility and diffusivity in the polymer increased [31]. The fractional free volume increases with temperature according to eqn 9.5, which provides more paths for water molecules to pass through the membrane. The increase of free volume in the polymer, and the micro-Brownian motion of the soft segment obviously increases the intermolecular gap enough to allow water vapor molecules to pass through the membrane [22]. With increasing the block length of the PEG component in the polymer, the WVP also increases (Fig. 9.9), due to the increased flexibility of the polymer and increase of hydrophilicity [22], which increases the interaction between water molecules and polymer chain segments (Fig. 9.10), and increases the permeability because permeability of non-porous membranes follows the law: sorption–diffusion–desorption. On the other hand, longer polymer chains of PEG originate larger polymer network holes that will also enable the water vapor molecules to pass through the membranes.

Moreover, when the experimental temperature reaches the soft segment crystal melting point, discontinuous density changes occur, which take advantage of micro-Brownian motion (thermal vibration). Micro-Brownian motion occurs within the membrane when the temperature rises above a predetermined activation point. The activation energy can be considered as the energy to 'loosen' the polymer structure, which is related to the change in thermal expansivity. An increase in temperature provides energy to increase segmental mobility, which increases the penetrant diffusion rate. As a result of this motion, more micropores are created in the polymer membrane which



9.9 Effect of block length of PEG on WVF at 35 °C.



9.10 Schematic representation of water molecule transport through a non-porous hydrophilic membrane (adapted with permission from Johnson L., and Samms, J., J. *Coated Fabrics*, 27 (July), (1997), 48 © Technolmic Publishing Co. Inc [16]).

allow water to escape. That is why the WVF curves for S_7 and S_8 increase sharply (Fig. 9.8), because of the confluence of hydrophilicity, increase of free volumes, and micro-Brownian motion in the membranes at the soft segment crystal melting point. But in the case of S_6 the increase of WVF is due to the confluence of hydrophilicity, and increase of free volume. On the other hand in the case of samples S_9, without hydrophilic segments, the WVF is very low as compared to S_7 and S_8, even as compared to S_6, because in these samples, increase of WVF with temperature is due to the increase of free volume and increase of saturation vapor pressure, which is the same in all cases.

So, in summarizing the experimental results and discussion of water vapor permeability of shape memory polyurethane films, we can say that a large change in water vapor permeability occurs at the transition point (glass transition temperature/crystal melting point temperature) due to the morphological change of the polymer membrane. In addition, the presence of hydrophilic groups in the polymer structure also enhances the permeability due to the increasing solubility of water vapor molecules in the membrane.

9.5 Future trends

The property of breathability is in great demand by today's breathable textile industry. The inherent desire is to create fabrics that will provide protection from water droplets while allowing water vapor to escape. The use of breathable textiles will undoubtedly continue to expand into apparel applications. Some commercial breathable textile products are already available in the market. Mitsubishi is testing a new breathable fabric in the United States. The fabric is called Dream Cloth [32]. It is designed to keep people warm in cool temperatures, and cool in warm temperatures. The fabric achieves this through a polymer coating that acts like human skin. The molecular structure of the fabric coating opens when the wearer becomes hot, thus allowing body heat and vapor to escape. When the temperature drops, the molecular structure closes to provide insulation against the cold.

With the advantages that shape memory polymers can offer in coating/lamination products, unparallel hand and drape will emerge and have important implications for sports and leisure-wear in the apparel markets. Forecasting future trends is always speculative, but we are confident for the future of shape memory polymer films in breathable textiles.

9.6 Acknowledgement

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10

Engineering textile and clothing aesthetics using shape changing materials

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10.1 Introduction

This chapter focuses on the Design/Technology interface (Stylios, 2003) for developing SMART textile materials. Textiles are capable of unique shape changing behaviour by incorporating shape formed alloys and/or polymers incorporated within their structure. These are called in the first case shape memory alloys (SMA) and in the second case shape memory polymers (SMP), and belong to the family of shape memory materials (SMM).

Other properties of SMMs include pseudoelasticity or recoverable stroke (strain), high damping capacity and adaptive properties which are due to their ability to reverse the transformation during phase transitions. SMMs can sense physical changes in their environment, such as thermal, mechanical, magnetic or electric. These physical stimuli make them to respond by transforming their shape, position, strain, stiffness, natural frequency, damping, friction and other static and dynamic characteristics.

This chapter will show how the shape changing behaviour of textiles is being achieved by programming SMA, or by spinning SMP and ultimately by developing them into yarns for incorporation into woven, knitted or other textile structures. Their shape changing ability and the possibility of engineering this shape change for SMART applications have inspired the aesthetics of new designs for interior textiles and knitted garments, and have contributed to new hybrid mood changing textiles for smart ambience.

10.2 Innovative design concepts in textiles and clothing

Consumers are increasingly becoming more adventurous in curiosity and taste and with increasing disposable income, are driving the design industry in different endeavours. There is an increasing interest in products that are not only visually and aesthetically well made, but that can also excite, surprise and entertain the user/wearer. Lifestyles are changing too, with less time on our hands, accessories and products that facilitate ordinary chores, or help us to save time become attractive. Blinds or screens that open and close by themselves to accommodate the amount of light or heat in an office or room, upholstery that changes colour and shape depending on our mood, garments that can self-iron are examples that illustrate the self-managing capabilities of some products that have raised interest from consumers and industry alike.

Technological advances are making these innovations possible. In recent years, there has been considerable interest in non-static designs, in textiles, in fashion as well as in textile art. With the advent of new materials such as chromatic dyes and pigments, which change colour under a given stimulus, phase change materials, which change temperature within their environment and shape memory alloys and polymers, design concepts can now be more dynamic and interactive with the user or wearer. We are in an era of 'SMART TEXTILES', which at the flick of a button, or with an environmental change, can change shape, colour, texture, pattern, drape and handle. This concept has been explored in the fashion community, e.g., with colour-changing garments and with designer fashion incorporating shape memory wires (Marks, 2001).

Dynamic and interactive designs are the result of increasing multidisciplinary collaborations, in particular between designers and technologists (Stylios *et al.,* 2005; Chan *et al.*, 2002). Corpo Nove (Italy) has already attempted the use of a shape memory alloy in a designer shirt which rolls up its sleeves when the body gets warm. Increasingly, multinational companies such as Philips and Siemens, which originally were more technology rather than design-based are investing more and more in design/technology products. Designers are gradually changing from being traditionally 'users of technology' to now having a fundamental understanding of many of the technologies that they use. This leads to design now being used for specific functions in addition to being a visual and aesthetic attribute. Photochromic patterns that visually warn the wearer of excessive UV exposure, texture and morphological changes in an interior textile office partition, which not only creates different aesthetic effects, but also provides a function such as increasing the airflow or reducing sound and noise are other recent examples of functional design technology.

10.3 The principles of shape changing materials and their end-uses

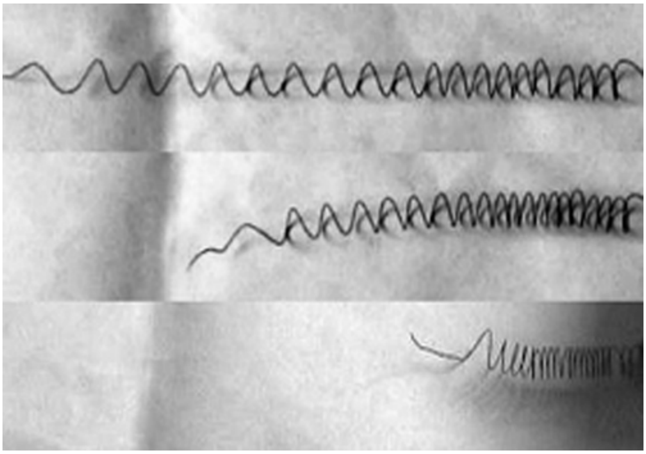
Shape memory materials are able to 'remember' a shape, and return to it when stimulated, e.g., with temperature, electrical current, UV light, etc. The most common types of such materials are shape memory alloys and polymers, but ceramics and gels have also been developed.

10.3.1 Shape memory alloys

The first shape memory effect was observed in a gold-cadmium alloy in the early 1930s, and it was only in the 1960s that nickel-titanium alloy, a cheaper non-toxic alternative, was discovered. To date, nickel-titanium is still the most popular SMA and has been used in numerous functional engineering applications. Other shape memory alloys include copper-based or iron-based type variations.

The shape memory mechanism in alloys is generally caused by two distinct structural states: an austenite phase (highly ordered phase at higher temperature, also called the parent phase) and a martensite (less ordered, lower temperature, deformable) phase. In general, heat or mechanically induced stress is able to cause a change in phase type, e.g., from martensite to austenite, or between variants of martensitic phases (de-twinning), which generates the shape memory effect (Panoskaltsis *et al.*, 2004). With heat for example, the material is able to change from the martensite to the parent phase, through diffusionless transformation, leading to a shape 'recovery'. Hence, provided that the material has been 'fixed' into a specific physical form in its high-temperature parent phase, at a lower temperature, it can be distorted, but will 'remember' the original form when reheated. Figure 10.1 illustrates the shape memory recovery process of a SMA spring.

An attractive feature of SMAs is that they enable a two-way shape memory effect, also known as the all-round shape memory effect (Otsuka and Ren, 2005). This allows for repeated cyclic applications as the material is able to remember a shape at two different temperatures. Alloys are able to recover a large proportion of their deformation (up to 100% of the original programmed shape). However, they exhibit low strain ranges (up to 8%) compared to polymers (Shaw and Kyriakides, 1995).



10.1 Shape memory recovery of SMA spring with time when T > 50 °C.

10.3.2 Shape memory polymers

The shape memory mechanism and effects in polymers are unique and different from those occurring in metals and ceramics (Liu *et al.*, 2004). The mechanism relies on a cross-linked structure at a molecular level. In the case of temperature-sensitive shape memory polymer, below glass transition temperature T_g the polymer is a stiff cross-linked network of chains, but above T_g, the network lends itself to a rubbery plateau state. The shape memory effect can be created by forming a shape while the polymer is in the rubbery state, and 'freezing' or 'fixing' this entropic state at a low temperature (Liu *et al.*, 2004; Ohki *et al.*, 2004). This frozen form can then be released only at a higher temperature.

Recently, the development of a UV-sensitive shape memory polymer has been reported (Borchardt, 2005). In this case, the mechanism is dependent upon the grafting of photosensitive groups into a polymer network shaped as required. The polymer is exposed to UV light, which causes the photosensitive groups to cross-link and fixes the new shape. Subsequent exposure to light of a different wavelength cleaves the cross-links and brings back the original shape.

The mechanism of shape recovery of SMP is dependent on the combination of a partially crystalline hard segment and a soft amorphous segment at the transition temperature T_g. Above T_g, the permanent shape can be deformed by the application of an external stress. After cooling below T_g, the amorphous segment is 'frozen' in a glassy non-crystalline state of high elastic modulus and hence obtains the temporary shape (Metcalfe Annick *et al.*, 2003). The material recovers to its permanent shape upon heating to $T > T_g$.

Shape memory polymers have some advantages over their alloy counterparts. They are lightweight, are able to withstand larger strains (up to 400%), possess a wide range of recovery temperatures, have low manufacturing costs and better processability (Yang *et al.*, 2005; Ohki *et al.*, 2004). For textile applications, when spun they are more flexible and can blend easily with other conventional yarns and woven and/or knitted structures (Chan and Stylios *et al.*, 2003b). Examples of shape memory polymers include segmented polyurethanes, poly(cyclooctene), poly(lactic acid) and poly(vinylacetate) blends (Liu *et al.*, 2002). A recent study of SMPs has been carried out by Hn (forthcoming).

10.3.3 Shape memory coatings

The area of shape memory coating (SMC) materials is new and reported developments are scarce. One promising SMC is reported by Stylios and Wan (2006) who have developed a highly adhesive resin coating solution by dissolving polyurethane SMP in dimethylacetamide.

10.3.4 Colour changing materials

Thermochromic materials change colour reversibly with changes in temperature. They can be made as semi-conductor compounds, from liquid crystals or metal compounds. The change in colour occurs at a pre-determined temperature, which can be varied. Current research involves the development of temperature-sensitive polymer-based pigments that visually and reversibly change colour at a prescribed temperature in the region of 15 to 35 °C. The temperature of the colour change (called the thermochromic transition) can be altered by the structure of the polymer-based pigment used and can be tailor made by chemical modification. In effect, thermochromic coated polymer films are thermal sensors that detect change of temperature with visual transformation.

With different constitutions of thermochromic and generic colour pigment, numerous colour variations can be produced. The thermochromic pigment can be incorporated into a coating solution for the film formulation or directly as paint with a special binder (such as PEG) for texture surface effects. Materials containing 0.1–1.0% by weight of thermochromic pigments in a host polymer have a visually retrievable, reversible thermochromic transition. The combination of SMM and thermochromic coating is an interesting area which produces shape and colour changes of the textile material at the same time.

10.3.5 Typical end-uses

Until recently, end-uses for SMMs were principally in the technical and functional engineering fields. SMPs and alloys have been used as heat-shrinkable devices, biomedical devices such as stents (Keiji, 2003) or other implantables and deployable structures. In the last ten years or so various companies developed new techniques for making SM textiles with some success (Kobayashi and Hayashi, 1990; Yoshida, 1991; Kitahira *et al.*, 1996; Butera *et al.*, 2004) and more recently, SMMs have started to find use in the fashion and clothing sector, with one of the first examples being the Corpo Nove shirt (Marks, 2001). There is also significant interest in using shape memory polymers as coatings for crease recovery and easy care apparel textiles, and for upholstery and other interior applications.

10.4 Technical requirements for shape changing textiles and clothing

10.4.1 Shape changing under stimuli

Many man-made and natural materials are naturally shape changing. A classic example is cotton, which expands when exposed to humidity and shrinks back when dried. Such behaviour has not been used for aesthetic effects because the changes, though physical, are in general not noticeable to the naked eye. In the case of shape changing textiles and clothing, a key requirement is to have a noticeable, visible shape changing effect, be it surface-bound, or form-bound. This consequently leads to two essential criteria: the efficacy of the material and the ability for the effect to be triggered as and when required.

In a woven, knitted or non-woven textile, the interactions between yarns and fibres contribute to the strength and mechanical properties of the fabric. With blended SMMs, these interactions can also act as a resisting force, to constrict the effect of the SMM. Hence for example, Chan and Stylios (2003a) found that in the case of wrap-spun shape memory polymer yarns, the twist of conventional fibres around a core shape memory filament prevented the core from performing its shape-changing function. The situation was further exacerbated when the yarn was turned into fabric. It is therefore essential that the shape changing 'force' is higher than the resisting forces in the textile structure.

The second criterion is the ability to be stimulated to the right level when required, or under normal conditions of use. Temperature-sensitive shape memory alloys and polymers can be programmed to respond at specific temperatures, which falls within a broad range. Programming however requires that the maximum effect be achieved under the temperatures of use. Other stimuli can also be used, e.g., electrical currents, magnetic fields or UV lights. Wang *et al.* (2004) found that the shape change in nickel-titanium alloys largely depended on the magnitude of the electrical current. For SMPs, the challenges of making the polymer conducting current are still to be met, but work is already in progress (Yang *et al.*, 2005). As for magnetic shape memory responses in alloys, they have been found to be highly variable, therefore posing a challenge for their applications (Heczko, 2005).

10.4.2 Problems associated with processability

Incorporating shape memory materials into textiles has been tried for over 15 years now, but many of the difficulties of turning the materials into textiles and clothing still exist. Alloys, due to their low strains, are difficult to weave and knit, because a certain amount of stretch in the material is required in order to interweave and inter-loop. With respect to aesthetic requirements, some novel woven or knitted structures require added flexibility for ease of production and suitability. Polymers, which have higher strains and lend themselves more to textile processing, are easier to turn into yarns, fabrics and clothing (Oohira, 1990; Terada, 1990). The textile assembly consisting of the shape memory materials must be able to be programmed, i.e., treated to train the material to remember a shape. If high temperatures are required (e.g. for some alloys), it may not be possible to treat the whole textile assembly, so the alloy has to be programmed prior to its inclusion into the textile structure. This can pose problems associated with the creation of specific effects. Chan and Stylios (2003a) have successfully pre-programmed and used SMA in textile fabrics as well as spun and programmed SMP into various textile woven structures for the first time.

10.4.3 Durability of shape changing effects

Durability of effects during use includes requirements for resistance to abrasion caused by ageing, wear and tear, but also good performance in cyclic repetition of the shape memory effect over a period of time. It is well known that shape memory alloys such as Nitinol can undergo deformation and shape reversing many times, but much less is known in the area of SMPs. Hysteresis and fatigue in cyclic loading of SMMs have been studied to some extent for metal alloys (Eggeler *et al.*, 2004). Among other parameters, temperature, microstructure and surface quality of the material inevitably affect their fatigue behaviour. Bhuniya *et al.* (2005) reported that the addition of small amounts of titanium to SMAs reduces their microstructural degradation caused by ageing. This is of interest for textile applications, where shape memory responses and reactions must be efficient for at least the estimated lifespan of the product in order to justify the costs.

10.4.4 Aesthetic degradation

Aside from performance, aesthetically, shape changing textiles should aim at having minimum visual and tactile degradation over time. This is particularly the case for products that will undergo harsher environmental conditions, e.g., interior textiles such as window blinds exposed to strong sunlight and environmental pollution. Nickel-titanium alloys are generally resistant to the environment and will not undergo corrosion. In the case of shape memory polymers, little is known about their long-term visual and tactile effects. Many polymers often experience brittleness, stiffness and colour change with ageing, in particular if exposed to harsh environmental conditions. This could impact on the visual effects, handle, comfort and drape of the textile characteristics which are particularly important for clothing.

10.4.5 Requirements for fashion and clothing

The requirements for fashion and clothing are slightly higher than for non-wearable textiles, in particular if the material is to be worn next to the skin and has to be washed. Chan and Stylios (2003a) and Winchester and Stylios (2003) highlighted the relatively harsh handle of the alloy and bulkiness of the shape memory polymer filaments, but also showed that this is not in itself a deterrent to the use of such material in textiles, as they can be used sparsely, but with significant visual and functional impact. They have also shown how blending with conventional or specialised yarns like elastane, can improve handle, tactile and recovery properties. Alloys pose a particular challenge for designers as they will provide the most dramatic shape memory effects, but also adversely affect drape, handle, touch and comfort.

10.5 Engineering textile and clothing aesthetics with shape memory materials

10.5.1 Extrusion of SMP

In a recent research project, a polyurethane-based SMP was used. The polymer pellets were dried prior to processing and extruded using an ESL Labspin 892 pilot-scale screw extruder into continuous monofilaments and multifilaments. The T_g of the polymer was 25 °C. The raw resin pellets were dried for eight hours in a hopper circulation oven at 80 °C until moisture was less than 0.03%. Without drying the resin, its viscosity becomes too low when melted, causing deformation by foaming, flashing and dropping at the nozzle. The temperature profiles of the machine suitable for processing of SMP yarn of 0.4 mm to 0.6 mm diameter using a die diameter of 1 mm, are as follows:

rear (feed zone): 170–180 °C
centre (compression): 175–185 °C
front (metering zone): 170–180 °C.

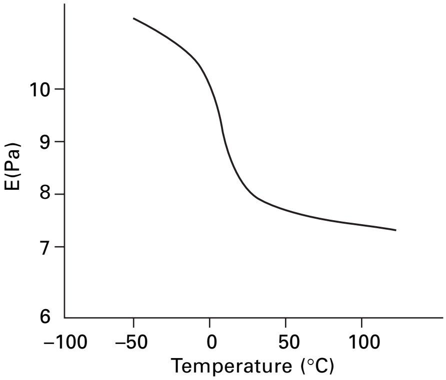
The key of this operation is to control the viscosity of SMP in the nozzle at the extrusion machine, while assuring uniform melting of the polymer. The viscosity of SMP is more temperature-dependent than traditional polymers, requiring stricter temperature and processing controls for extrusion. In order to control the diameter of the SMP yarn, the extrusion rate of yarn has also to be regulated.

Table 10.1 shows the characteristics of the fibre.

It should be noticed that the recoverable force of the pre-deformed ‘frozen’ SMP itself is ascertained as weak since the soft state of SMP is caused by the

Table 10.1 Fibre characteristics

Fibre diameter	0.10–0.34 mm
Tensile stress	0.1–0.8 kN/mm^2
Elongation at break	260–980%



10.2 Dependence of elasticity modulus of SMP on temperature.

rise in temperature. Several physical properties of SMPs other than the SME are also significantly altered due to external variation in temperature, particularly at the glass transition temperature of the soft segment. These properties include elastic modulus, hardness and flexibility. As an example, temperature dependence of elasticity modulus E′ of SMP is illustrated in Fig. 10.2, in which the elastic modulus of an SMP is changed dramatically when heated above the glass transition temperature of the soft segment.

10.5.2 Yarn and fabric formation

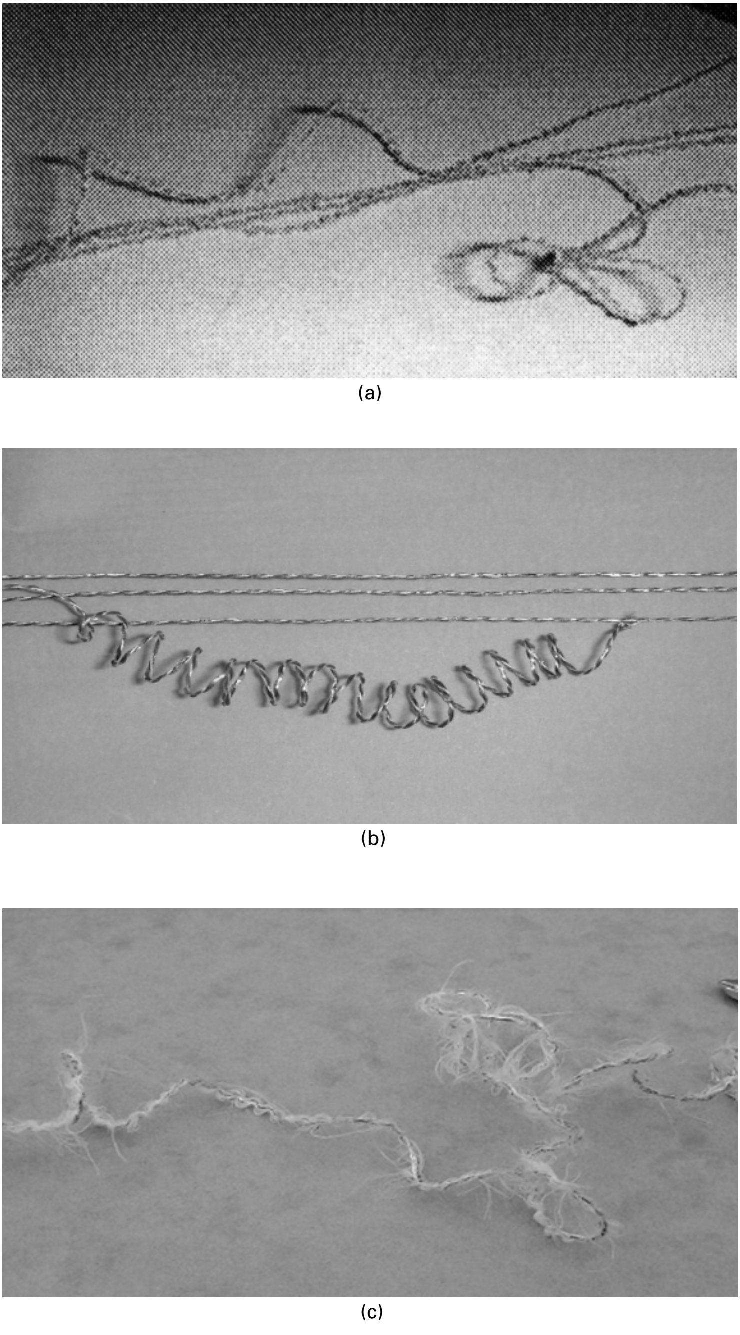
Using a Gemmel and Dunsmore Fancy Wrap Spinner, extruded SMP fibres were used as:

- core filaments in wrap-spun yarns
- blend material with other fibres (polyester, viscose and Lurex)
- filaments in unblended yarns.

The yarns were woven and knitted into three-dimensionally changing structures. Knitting and weaving of the material did not raise difficulties, as in the case of knitting the SMA. A range of SMP yarns and complex fabric structures made therefrom were designed and made up, as shown in Fig. 10.3.

10.5.3 Shape programming

Unlike SMA, which has to be programmed before incorporation in the textile structure because of the high treatment temperature, SMPs are treated after their incorporation into yarns and fabrics. It is therefore possible to program the shape of the whole fabric for the shape memory effect. The treatment in this particular case was performed at a temperature of 50 °C. The shape



10.3 SMART yarns; various yarn composite blends with SMP.

memory effect on the fabric was clearly visible upon application of an external heat source such as a fan heater or a hair dryer.

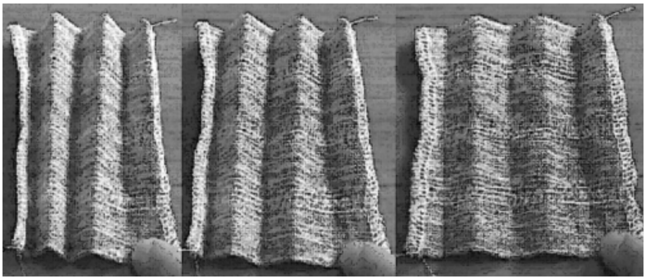
10.5.4 SMP effects in fabrics

The main visual effect of the fabrics comes from the fact that areas containing the SMP are highly deformable, but upon heating, contract back to their original shape (Chan and Stylios, 2003b). Visual textural and structural effects that were explored from this deformation were:

- opening and closing of gaps within the structure of the fabric
- surface movements, including extended floats
- honeycomb structures
- double cloth elevated effects.

It was found that the effect of SMP as a core component in wrap-spun yarns was less pronounced, possibly as a result of the conventional fibres restricting the recovery movement of the polymer.

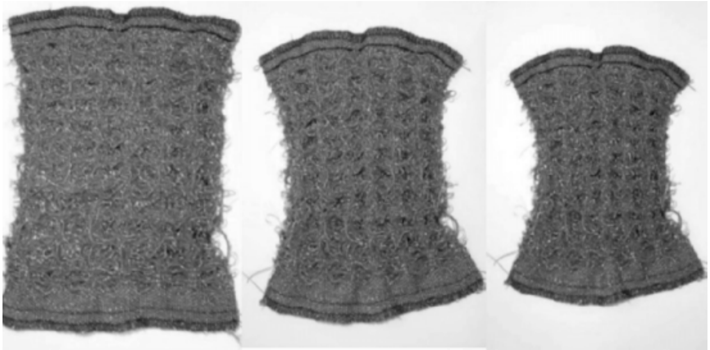
Figure 10.4 illustrates shape memory performance of SMP textile samples with uniform and densely woven SMP yarn of 0.4 mm diameter in the fabric structure. To observe the SME in the textured fabrics, the SMP composite is covered with two sheets of aluminium foil and deformed into the shape illustrated in Fig. 10.4(a) under higher temperature. The sample is then placed in a fridge under a mechanical constraint. The SMP filament recovers to its original shape of being flattened at a high temperature from being deformed at a low temperature upon heating to $T > T_g$, which allows the shape of the fabric sample to vary with environmental temperature. This is because the straightened state of SMP yarn at high temperature originates from the extrusion state when leaving the nozzle of the extrusion machine without any further shape memory training. Below the transformation temperature T_g, the bend shape of this textile is hibernated to provide a



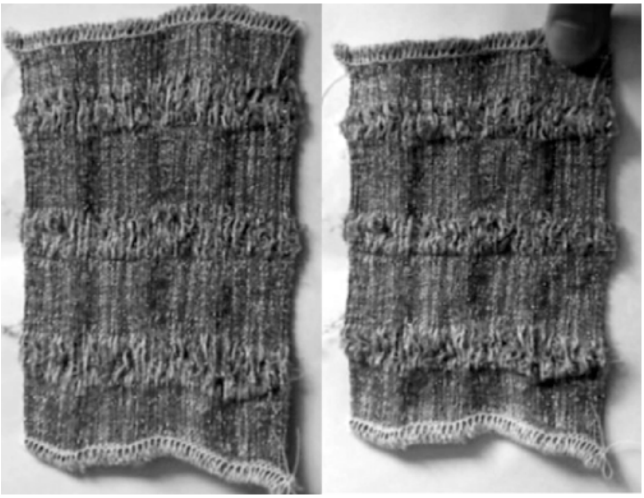
10.4 Shape memory recovery of SMP composite woven uniformly and densely of SMP yarn at 50 °C with recovery time (a) 0 sec, (b) 15 sec, (c) 30 sec.

support force for the deformed state. After the specimen is heated up over the transformation temperature T_g, the hibernated SMP filament becomes soft and recovers to the original flattened shape. However, the shape memory effect in the SMP filament is mono-directional and it is difficult to perform an invert shape variation procedure. The problem is solved by adding some reinforcement yarn of high elastic modulus to the SMP matrix.

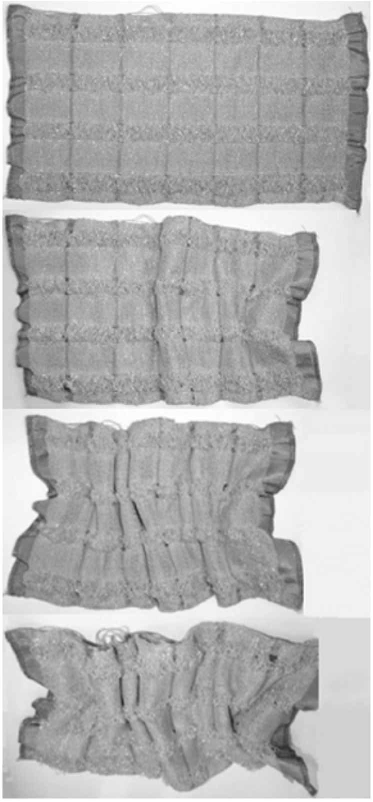
Conventional yarns of different material performance can be blended and woven with SMP yarn as illustrated in the samples in Figs 10.5, 10.6 and 10.7. The SMP filament was woven spaciously and loosely along the weft to allow room for the SME to take place. In contrast with the sample shown in



10.5 Shape memory recovery of SMP composite loosly woven fabric with SMP yarn at 50 °C with recovery time (a) 0 sec, (b) 30 sec, (b) 60 sec.



10.6 Shape memory recovery of SMP composite loosely woven fabric at 50 °C with recovery time (a) 0 sec, (b) 30 sec.



10.7 Shape memory recovery of SMP composite loosely woven fabric with flexible yarn at 50 °C with recovery time (a) 0 sec, (b) 30 sec, (c) 60 sec.

Fig. 10.3, the composite structure freezes the fabric at the flattened state. The initial flat shape of these SMP composites is fixed by exerting an external stretch force when the sample is in a freeze state. The SME occurs similarly from its original flattened state at low temperature to an embossed matrix with convex edges state, when being contracted at a high temperature. In this case, complete contraction occurs because the elastic modulus of the SMP yarn decreases dramatically when the environmental temperature is over the T_g temperature.

The recovery process may also be described as metamorphic in which the polymer exhibits a gradual shape variation during transformation. However, fabric designs based on SMP yarn blended with various kinds of flexible and light yarns can show interesting and aesthetically appealing effects, as shown in Fig. 10.7. The change of fabric shape depends on fabric design and SMP specific training at a given external temperature. It is apparent that shape memory design and training can create a number of aesthetic appeals with different texture yarns, showing significant shape change in response to environmental variation. More work is expected to be carried out in fabric design with reinforcement of high elastic modulus incorporated into SMP yarn to improve recovery.

10.5.5 Potential applications and limitations

Trained correctly, SMP can be used in a number of textile applications as SMART materials. The high levels of deformation and 'stretch' possible with SMP, in combination with their lower bending rigidity, make the material suitable for textile processing such as knitting and weaving to form fully flexible structures with good texture and handle. Also, the handle of the SMP, being softer and more flexible than SMAs, renders the material ideal in applications where comfort and drape are important, e.g., fashion and clothing, upholstery, sportswear, protective clothing or medical garments. Other application areas include interior textiles (e.g. blinds, partitions and curtains that can open or close depending on temperature) and medical textiles (e.g. responsive wound dressings or supporting materials). However, designs have to take into account the fact that SMPs have slower response than SMAs.

10.5.6 Programming SMAs

SMAs are normally 'trained' to remember one or two particular shapes while they are in the austenite phase. In recent work reported here, nickel-titanium (Ni-Ti) SMA wires of 0.1–0.3 mm (transformation temperatures $A_s = 25.5$, $A_f = 46.5$, $M_s = 10$ and $M_f = -14.5$ °C measured by DSC) were trained and programmed by a thermomechanical process involving heating the 'shaped' alloy for up to four hours at 650 °C in an inert atmosphere, followed by quenching in water. It is demonstrated that a solution treatment at 650 °C/60 minutes and ageing treatment at 380 °C/100 minutes yields an M_s of about 14 °C, while ageing treatment at 480 °C/100 minutes yields an M_s of about 20 °C. The variation is consistent with the formation of lenticular Ti_3Ni_4 precipitates. When the specimen is annealed at a temperature lower than 400 °C, the Ti_3Ni_4 precipitate particle is fine and the dispersion density is high, so the precipitate Ti_3Ni_4 has great coherence with the matrix. On the contrary, when annealed at a temperature higher than 400 °C, the precipitate Ti_3Ni_4 grows up and the low dispersion density destroys the coherence between Ti_3Ni_4 and the matrix (Nishida and Wayman, 1984; Scherngell and Kneissl, 1999). As conventional textile materials are not able to withstand the high temperatures required for the programming, use of SMAs in textiles normally requires programming of the alloy before yarn spinning, weaving or knitting.

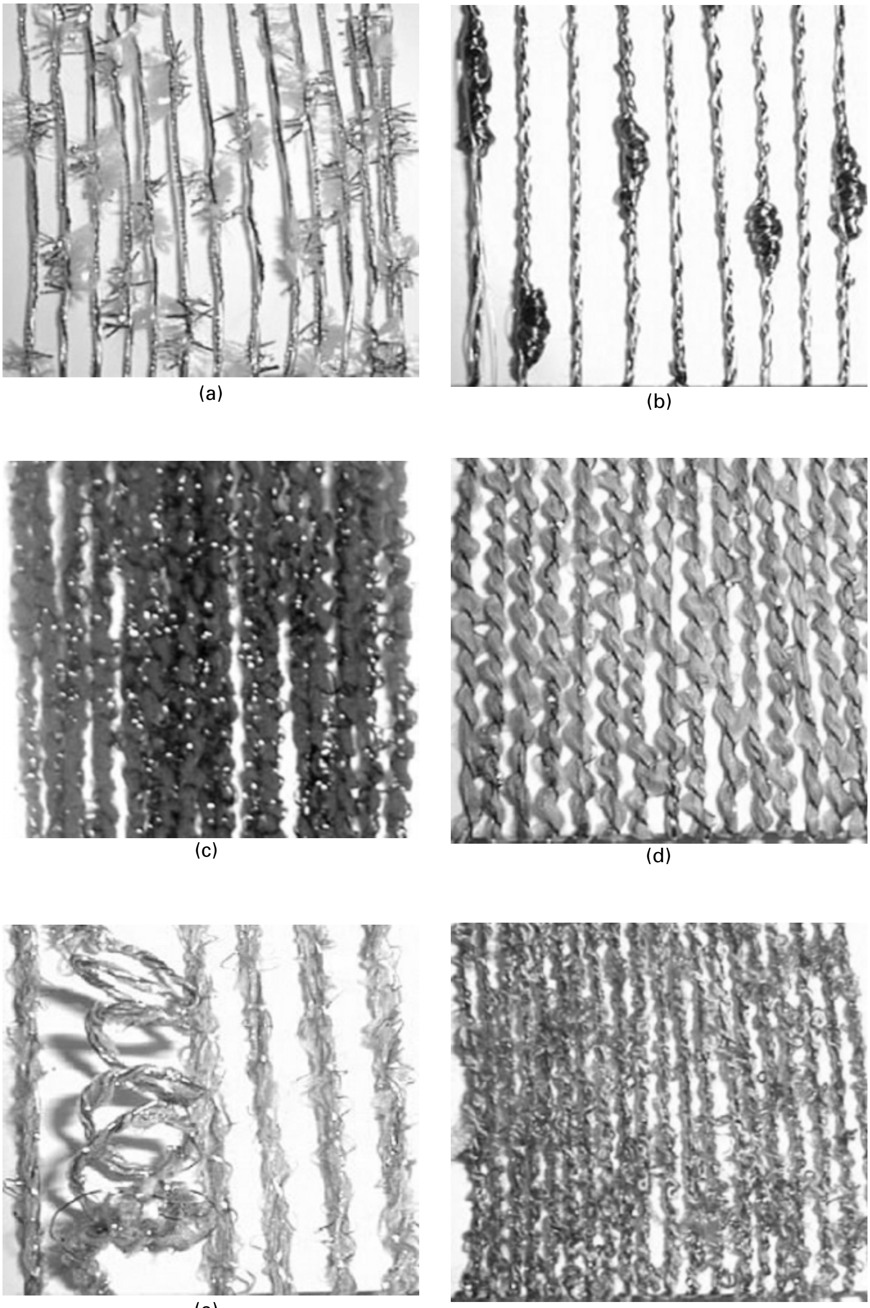
The shape memory recovery of a textile that contains a trained SMA spring with varied temperature, in which the shape of the fabric changes under the influence of the trained SMA spring incorporated into the fabric structure has been investigated. In this case, the fabric can display a two-way shape memory effect when the spring is trained in such a way. Since the training of two-way SME springs is carried out before the spring wire is woven into a fabric structure, various fabric structures with different yarn textures, have been developed. The trained SMA wire may be engineered to enhance the aesthetic appeal of fabrics or clothes, showing the potential for significant shape change in response to environmental variation. An example of a potential application is the creation of an intelligent window curtain with self-regulating structures changing under a range of temperatures.

10.5.7 SMAs in yarns

Yarns can be designed with trained Ni-Ti SMA wires as core component, wrapped with conventional fibres such as polyester, viscose and polyamide. A range of yarns with different twist levels and fibre content have been produced in a recent work using a Gemmel and Dunsmore Fancy Wrap spinner, shown in Fig. 10.8. The level of coverage was found to be important in order to prevent the alloy, as the core structure, protruding from the yarn during the development of the shape memory effect. Yarns were optimised for maximum stability during mechanical deformation by altering the yarn specifications particularly their twist level.

10.5.8 Fabric development

Experimental fabrics have been made of SMA wire and/or of SMA wrapped-spun yarns. Woven structures consisting solely of untrained SMA wires are programmed after weaving and trained as a whole structure. Knitting a structure consisting entirely of SMA wires is more complex due to the low extensibility of the wire which creates difficulties in loop formation, stability and regularity. In the case of knitting wrap-spun SMA/fibre yarns, it was found that due to high stiffness and low tensile properties of the yarns, the process is significantly affected by the properties of the core SMA and hence complex structures were not possible. This was further prevented by the fact that the balance of the core/wrap structure could be easily disrupted during loop formation. Knitted structures consisting of selected areas of the core-wrapped yarns were found to be more stable. For woven fabrics, the wrap-spun yarns lend themselves for handloom weaving more easily, and various interesting structures have been produced.



(a)

(b)

(c)

(d)

(e)

(f)

10.8 SMART yarn blends with SMA.

10.5.9 Utilising the SMAs aesthetic effects

A range of textured and sculptured woven and knitted fabrics have been designed and produced. The following three-dimensional concepts have been developed using the alloy's shape memory properties as the basis for imparting physical changes in the fabric structure:

- movement in the fabric or on the fabric surface, e.g., visual wave effects and other textural changes on the surface of the fabric
- opening and closing of apertures in the fabric structure to alter properties such as opacity, insulation, diffusion of light, and air flow
- accordion-style opening and closing of the fabric structure, to create structures that can open and close, e.g., for interior screens.

By training the alloy to remember a specific shape in the deformable martensite phase, shape memory fabrics can be produced. When temperatures increase, the alloy changes from the martensite phase to the austenite one, and reverts to the shape that it was trained to remember. This creates structural and textural changes in the yarns and in the fabric. The changed structure will retain its shape until mechanically deformed again when fabric cooling takes place (Chan and Stylios, 2003b).

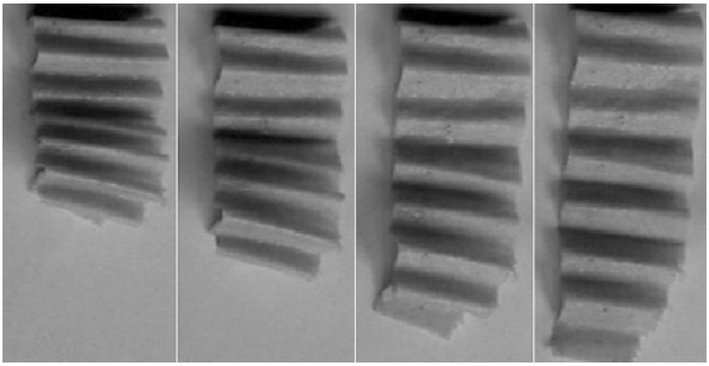
10.5.10 Potential exploitation and limitations

The exploitation of SMAs in SMART textiles relies on two main factors: the ability of SMAs to change shape upon the application of a stimulus such as heat or an electric current, and the flexible structure of woven and knitted fabrics. In the past, SMAs have been used in a number of non-textile applications, ranging from simple day-to-day items such as flexible frames for eyewear and coffee-pot thermostats, to high-performance devices such as vascular stents, medical anchors and guides and orthodontic braces. With the possibility now to incorporate them within a flexible textile structure, SMAs can find applications in the home and furnishing sector, clothing and sportswear sector, geotextiles, etc., where the shape changing effect can be triggered either by a change in ambient temperature, material temperature, or on the application of a small voltage.

Using alloys as composite textile structures, shape changes can be facilitated, particularly because of the high recovery properties. On the other hand, although SMAs can be used in selected areas only, they still add weight to the structure, and because of their stiffness, can have a detrimental effect on drape and comfort.

10.5.11 Shape memory coatings

SMCs pose most interesting possibilities due to their ability to be coated on existing textiles without the need for knitting or weaving them into the



10.9 Shape memory recovery of fabrics coated with SMP when $T > T_g$ (a) 0 sec, (b) 15 sec, (c) 30 sec, (d) 45 sec.

structure. Figure 10.9 shows shape memory recovery of fabric samples coated with SMP polyurethane. The SME may be trained from being flat at high temperature to being bent at low temperature, tailored to suit specific ranges of environmental temperatures. Observations revealed that SMP layered fabric have stronger shape recoverability compared with single layer shape memory woven fabrics, and therefore permit more flexibility in shape memory design, especially for SMP layers coated on stiffer fabrics (Wan and Stylios, 2004). The increment of shape memory recovery force in the textiles is due to a strong cross-linking of the fabric matrix that consists of high elastic modulus yarns. SMP reinforced with the matrix fabric having higher elastic modulus exhibits higher recoverability with the application of heat, which could be of great benefit to SMART textiles. In addition, when combined with reversible colour change pigment, intelligent hybrid coatings may be created to demonstrate a number of SMART functions, such as shape and colour change, in response to variations in environment temperature.

10.6 Aesthetic interactive applications of shape changing smart textiles

10.6.1 Textile art

One of the main areas where the characteristics of SMMs can be used purely for aesthetic and interactive purposes is in the area of textile art and design. Displays, 3D structures, flat panels and other forms of textiles including SMPs and alloys have a strong element of interaction between the viewer or the environment and the artwork. Krähenbühl for example utilised SMAs to create sculptures that react to wind and temperature (Gotthardt and Krähenbühl, 2005). Similar concepts can also be used in flexible textile art.

10.6.2 Fashion

In the fashion world, a number of aesthetic interactive effects can be incorporated in clothing and accessories, including shoes, bags, gloves, and the like. Corpo Nove has already illustrated the use of SMA in a shirt that automatically rolls up its sleeves when it is warm (Marks, 2001). Although this is, strictly speaking, not aesthetically driven, it does illustrate the potential for visual impacts. The development of ‘mouldable’ or ‘reformable’ fashion items that can be folded, twisted and changed into a desired shape when worn, and that will spring back to their original shape when stimulated is an interesting concept for the personalisation and customisation markets. Likewise, the developments of wearable items that, upon a flick of a button, can change shape, length, size, or other dimensional feature are interesting concepts to explore. The sportswear industry has already expressed interest in shape memory shirts that can open or close (macroscopically or microscopically) with body temperature in order to act as a heat and moisture management system, and also have an aesthetic visual effect. However, in addition to aesthetic and functional properties, SMMs can also be engineered for sensory and psychological effects. As an example, Winchester and Stylios (2003) demonstrated the use of shape memory alloys and polymers to create fabrics that can have interesting visual surface movements for knitwear, as shown in Fig. 10.10.

10.6.3 Interiors

Another area where the shape changing characteristics can be capitalised is in the interior textile industry, where again, the duality of the properties (aesthetic and functional) can be explored (Chan and Stylios, 2003a). Partitions, wall hangings and panels, window blinds, etc. with the ability to change

10.10 SMART knitted and woven structures for garments.

10.11 SMART interiors.

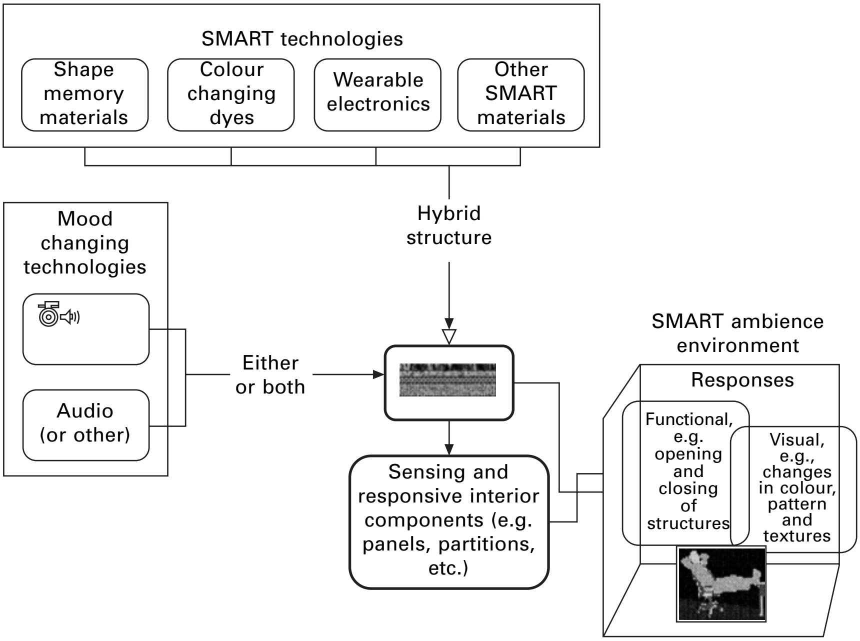
shape, texture and structure can create functional effects (more light, more air, more sound, etc.), but can also be used as decorative elements to interact visually and sensorily with people, Fig. 10.11. As illustrated by Chan and Stylios (2003a), the combination of woven 3-dimensional effects with shape memory properties creates exciting interactive visual effects with a huge potential for interior products.

10.7 The concept of mood changing textiles for SMART ambience

10.7.1 Introduction

SMART materials have been used for their functionality in the medical, aerospace, automotive fields and the like. Nowadays SMART material technologies (including SMMs, chromatic dyes and pigments, thermoelectric films and wearable electronics) are being optimised to explore the concept of SMART ambience, where an interior environment can respond interactively to the needs of users. A flexible composite matrix material integrating aesthetics and functionality is currently being developed by Stylios (2005). Focusing particularly on enhancing the functionality and aesthetics of SMART materials, this new field will bring a strong element of innovation to the interior and technical textiles industry.

Characteristics, properties and responses are being optimised for interior environment control both following moods and feelings through audio signal conversion technology in the first instance for interactivity. Based on the end-use requirements, this explores and combines several categories of SMART materials to create innovative hybrid architectures of flexible matrices. It tries therefore to create SMART structures, systems and prototypes with tailor-made functionality and aesthetics (Fig. 10.12) combining mood-changing technologies with SMART technologies for the development of a SMART ambience.



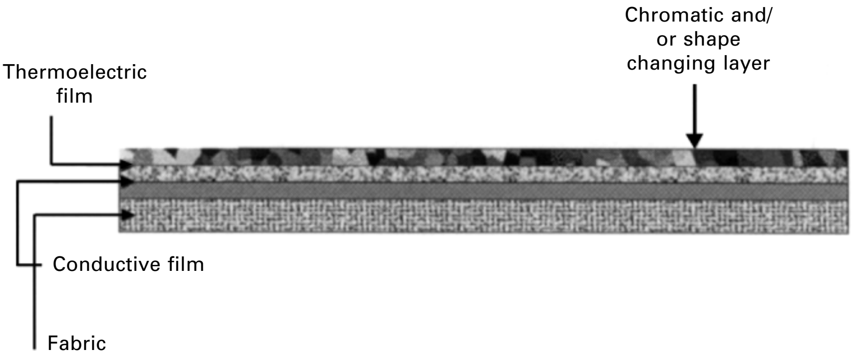
10.12 Combining mood-changing technologies with smart technologies for the development of a SMART ambience.

10.7.2 Technology approach

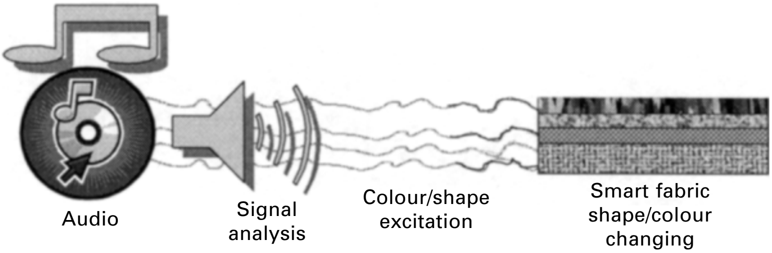
A new generation of hybrid structure(s) that can be used for interior components such as panels, partitions, and the like is being developed. The structure(s) are based on SMART technologies, integrated with mood changing technologies, Fig. 10.12, so that a new concept of a SMART ambience environment can be established.

Responses include both visual and functional changes in the structure, as a result of mood/physiological changes, or on command. For example a new hybrid composite matrix architecture, shown in Fig. 10.13 or structures that can change colour, pattern and/or texture can be created with the combined use of chromatic materials and SMMs. Colour and pattern effects are being imparted by chromatic materials. Texture and shape changes, e.g., changes in the openness and closeness of a structure, are being developed using shape memory polymers or alloys. Beside visual effects, functionally is possibly by changes of the shape memory which in turn can change the degree of air flow (hence temperature), improve privacy between partitioned areas and sound-absorption properties.

Upon command changes to the structure can be triggered by sending a signal to the structure, which then triggers these changes. Mood-dependent changes can be triggered in several ways, and are now being explored. The



10.13 SMART fabric architecture.



10.14 SMART fabric architecture mood selectable (SFAMS); mood changing SMART fabric matrix capable of changing shape and colour depending on personal moods.

first approach is by integrating audio output such as vocals directly to the structure through voltage by breaking the signal into primary colours and shapes Fig. 10.14. Another approach is by a webcam positioned on an office computer that can pick up facial expressions and detect typical moods (stress, happiness, sadness, etc.). Upon detection of these moods, specific changes in the SMART hybrid structure can be programmed to take place. In another approach, an inconspicuous wearable device (e.g. a wristband) with small sensors wirelessly connected to a central processing system can be used to detect physiological changes (body temperature, skin resistivity, heart rate, etc.) related to moods. The device can then transmit commands to the SMART hybrid structure to change. Finally and simply the environment can change at will by a switch or a computer selection by the user.

10.8 Summary

Recent advances in shape memory alloys (SMAs) and shape memory polymers (SMPs) have inspired people to create SMART textiles with self-regulating structures and performance in response to environmental variations, which constitutes a new field in the scientific frontier of SMART materials. By appropriate shape memory training of SMA and SMP, fabric designs can be engineered to enhance their functionality and particularly the aesthetic appeal of new textiles and clothes by significant shape change in response to environmental variation. Main technologies include the training procedures for shape memory effect (SMEs) in SMAs and SMPs, the regulation of phase transformation temperatures in SMAs, the manufacture of SMP yarns and SMP coatings for the requirements of new fabric design. Further attention is also paid to the combination of SMP or SMA with conventional yarn blends engineered to promote a given SME. Finally a hybrid SMART fabric architecture has been described and discussed for the next generation of mood changing textiles applied to SMART ambience.

10.9 Acknowledgement

I wish to acknowledge staff and students who have made the fascinating world of shape changing textiles possible; Dr T Wan, Dr Y Chan Vili, Dr S Lam Po Tang, Mr A McCullough and Mr S Wallace.

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