

SHAPE MEMORY POLYMERS

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1.Shape Memory Effect:

Consider the following example :

A dent is formed on a material by mistake . Consider the case when hair dryer is blown over it and amazingly the dent disappears . The effect the material showed is the shape memory effect. Shape memory effect is the property of a material to gain back its original shape when activated with suitable conditions .

2.Classification of the materials showing shape memory effect:

The materials showing shape memory effect can be classified as :

- (a)Shape memory alloys (SMA)
- (b)Shape memory Ceramics
- (c)Shape memory polymers
- (d)Shape memory gels

(a)Shape memory alloys (SMA):

Shape memory alloys exhibit the shape memory effect based on the martensitic transition . Here , the martensite phase is obtained by cooling the system from a higher temperature to a lower temperature . The high temperature phase is called the AUSTENITE which shows cubic symmetry and the low temperature phase is the martensite . The martensite phase can be deformed to upto 8 % and the deformation can be recovered just by heating the material to get the austenite phase .

(b) Shape memory Ceramics:

Certain ZrO_2 ceramics undergo a transition from tetragonal to monoclinic structure like a martensitic transition thermally or by the application of stresses . These ceramics are called Martensitic Ceramics.

(c) Shape memory polymers (SMP's):

The polymers which exhibit shape memory effect are called shape memory polymers . The mechanism of shape memory polymers are entirely different from that of shape memory alloys. The shape memory polymers depend largely on the glass transition temperature for the shape memory effect.

3. Glass Transition Temperature(T_g):

T_g is the temperature below which molecules have little relative mobility and are in a glassy state. T_g is usually applicable to amorphous phases. Above the T_g, secondary bonds between the polymer chains become weak in comparison to thermal motion, and the polymer becomes rubbery.

4. Thermodynamic aspects of shape memory polymers:

(a) Chain Conformation of Linear, Amorphous Polymers:

In the amorphous state, polymer tends to take the most random conformation as it is the most probable conformation for the same internal energy. The entropy is given by

$$S = k \ln w \quad \dots \text{Eq.1.}$$

where k is the Boltzmann constant and w is the probability of the most probable conformation.

(b) Transition from the Glassy State to the Rubber-Elastic State

In the glassy state all movements of the polymer segments are frozen. The transition to the rubber-elastic state occurs upon increasing the thermal activation, which means that the rotation around the segment bonds becomes increasingly unimpeded. This situation enables the chains to take up one of the possible, energetically equivalent conformations without disentangling significantly. The majority of the macromolecules will form compact random coils because this conformation is entropically favored and, as a result, much more probable than a stretched conformation.

In this elastic state a polymer stretches in the direction of an applied external force. If the tensile stress is only applied for a short time interval, the entanglement of the polymer chains with their direct neighbors will prevent a large movement of the chain. Consequently, the sample recovers its original length when the external stress is released. In this way, the sample shows a kind of memory for the nonstretched state. This recovery is sometimes called "memory effect", and is based on the sample's tendency to return to its original, most randomly coiled state that represents the most probable state.

However, if the external tensile stress is applied for a longer time period, a relaxation process will take place which results in a plastic, irreversible deformation of the sample because of slipping and disentangling of the polymer chains from each other. The tendency of the polymer chains to disentangle and to slip off each other into new positions enables the segments to undergo a relaxation process and to form entropically more favorable random coils.

In a similar way, an increasing rise in temperature above the glass transition temperature favors a higher segment mobility and a decrease in the mechanical stress in the elastic material being stretched by an external force.

(c) Entropy Elasticity

The described slipping or flow of the polymer chains under stress can be stopped almost completely by cross-linking the chains. The cross-linkage points act as anchors or permanent entanglements and prevent the chains from slipping from each other. The cross-links can either be chemical or physical. They contain physical netpoints. The highest thermal transition T_{perm} is related to the hard-segment-forming phase. If this thermal transition is not exceeded, these domains will stabilize the permanent shape by acting as physical netpoints in the material.

Besides the netpoints, networks contain flexible components in the form of amorphous chain segments. If the temperature is above the glass transition, then the networks will be elastic. They show entropy elasticity and can be stretched with a loss of entropy. The distance between netpoints increase during stretching and they become oriented. As soon as the external force is released, the material returns to its original shape and gains back the entropy lost before. As a result, the polymer network is able to maintain the mechanical stress in equilibrium.

(d) Molecular Mechanism of the Shape-Memory Effect of Polymers:

At temperatures above T_{trans} the chain segments are flexible, whereas the flexibility of the chains below this thermal transition is at least partly limited. In the case of a transition from the rubber-elastic or viscous state to the glassy state, the flexibility of the entire segment is limited. If the thermal transition chosen for the fixation of the temporary shape is a melting point, strain-induced crystallization of the switching segment can be initiated by cooling the material which has been stretched above the T_{trans} value. The crystallization achieved is always incomplete, which means that a certain amount of the chains remains amorphous. The crystallites formed prevent the segments from immediately reforming the coil-like structure and from spontaneously recovering the

permanent shape that is defined by the netpoints. The permanent shape of shape-memory networks is stabilized by netpoints, which are the phase with the highest thermal transition at T_{perm} . The memory effect mentioned in earlier section is not a shape-memory effect. In the polymer, hard segments act as net points and the soft phase is the switching segment which helps in fixing the temporary shape .

5. Some Examples of shape memory polymers:

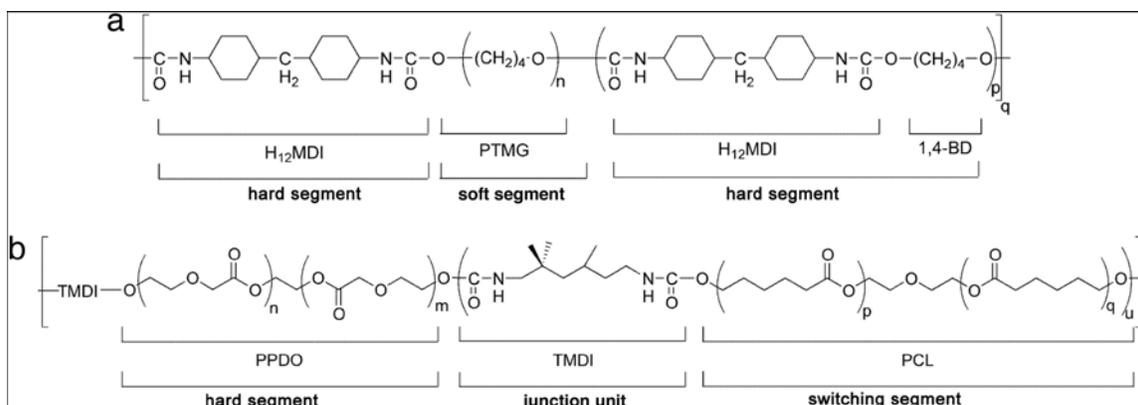


Fig. 1. shape-memory polymers showing the different hard and soft segments (a) Polyether urethane TFX (28), which is synthesized from methylene bis(*p*-cyclohexyl isocyanate) (H₁₂MDI), 1,4-butanediol (BD), and poly(tetramethylene glycol) (PTMG). (b) Multiblock copolymer PDC. PPDO, poly(*p*-dioxanone); TMDI, 2,2(4),4-trimethylhexanediisocyanate; PCL, poly(ϵ -caprolactone).

6. SYNTHESIS OF SHAPE MEMORY POLYMERS:

Preparation of Polyactide based urethane:

(i) Materials required :

l-lactide, 1,4-Butanediol(BDO) , stannous octate (Sn(Oct)₂), Hexamethylene diisocyanate (HDI) , toluene which is dried over Na wire and distilled before use , Ethyl Acetate which is dried over CaH₂ before use .

(ii) Preparation of poly(l-lactide) diol (HO-PLA-OH)

l-lactide was recrystallized in ethyl acetate for three times. It was then added to a glass container which had been flame-dried and equipped with a magnetic stirring bar. A toluene solution of 1,4-Butanediol(BDO) and Sn(Oct)₂ (0.3% of the BDO, mol/mol) was then transferred. An equal amount of toluene was then injected into the container. The reaction vessel was immersed into a thermostatic oil bath maintained at 125 °C for 24 h. The reaction product was precipitated into ethanol, filtered and dried at 40 °C in vacuum for 48 h.

(iii) Preparation of poly(l-lactide) polyurethane (PLAU)

A certain amount of the above prepared poly(l-lactide) diol (PLA diol) was dissolved in double volume of toluene and heated at 75 °C for 20 min. Sn(Oct)₂ (1% of the PLA diol, mol/mol) in dried toluene and a given amount of Hexamethylene diisocyanate (HDI) were added to the solution. After stirring for 10 min at 75 °C, 1,4-butanediol (BDO), the mole number of which was equal to the molar difference between HDI and PLA diol, was added and the reaction mixture was stirred for another 6 h. The polymer was isolated by dissolving the reaction mixture in chloroform followed by precipitation in ethanol.

Thus the poly(l-lactide) polyurethane (PLAU) is prepared.

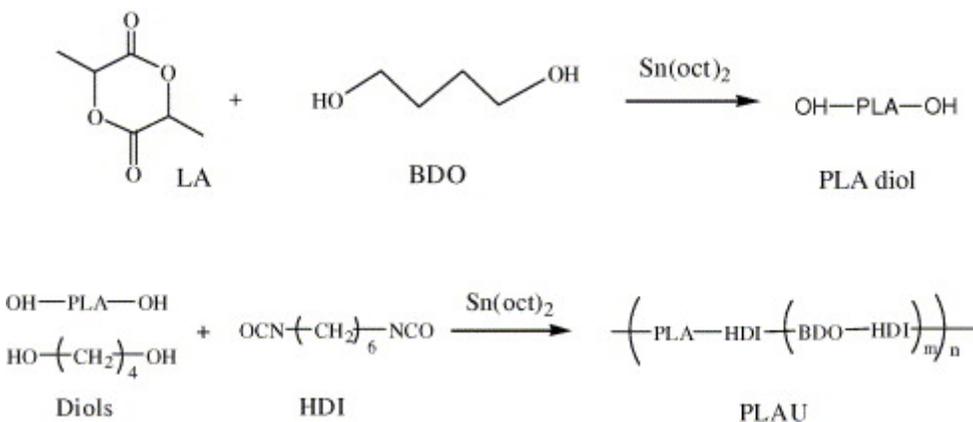


Fig 2. Schematic showing the synthesis of poly(l-lactide) polyurethanes.

7. Changing the Properties of materials :

Modifying the glass transition temperature(T_g): One way of changing the glass transition temperature is by immersing the shape memory polymer in water.

mechanism by which Tg is changed :

when shape memory polymer is immersed in water , the water molecules are absorbed . The absorbed water molecules can be characterized into two parts namely , free water and bound water .The free water molecule is formed when it bridges the gap between the hydrogen bonded N-H and C=O groups as shown in the diagram as site 'a' . This loosely bound water molecule directly weakens the hydrogen bond . The bound water molecule is formed when the absorbed water molecule forms a double hydrogen bond with two already hydrogen bonded C=O bonds as shown as site 'b' . the water in site 'b' is more tightly bound than the water in the site 'a' .

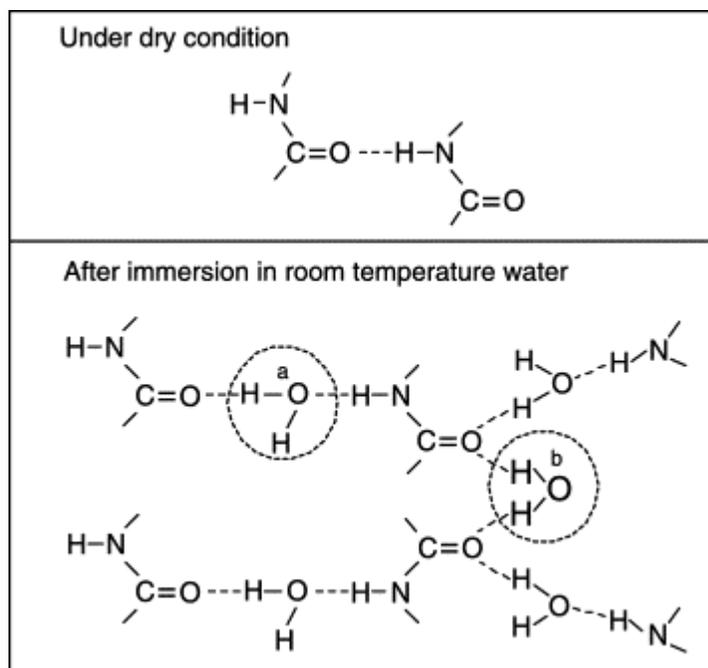


Fig. 3 Effects of water on the hydrogen bonding in polyurethane SMP

With the immersion time in water increasing the amount of absorbed water also increases and it is found that the amount of free water absorbed is always more than the bound water.

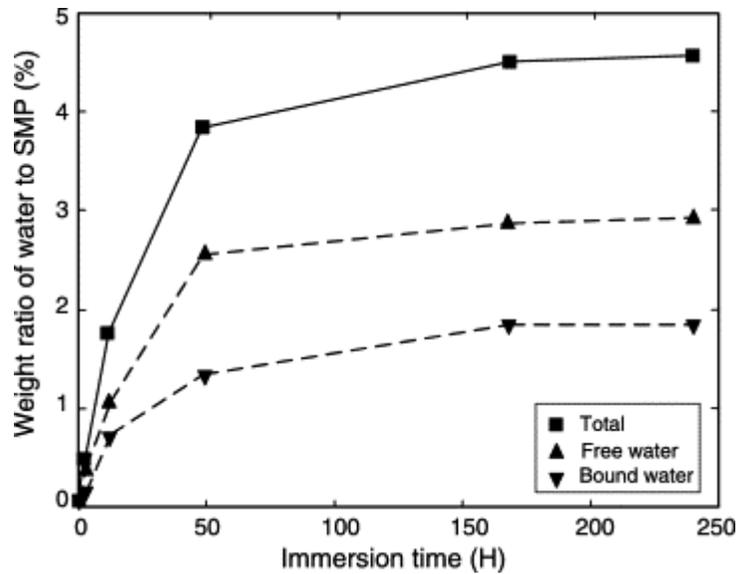


Fig. 4. Ratio of water to SMP in weight vs. immersion time.

As the immersion time increases, the glass transition temperature decreases. This property of reduction of the glass transition temperature can also be used for the activation of a shape memory polymer as illustrated in section 8(e).

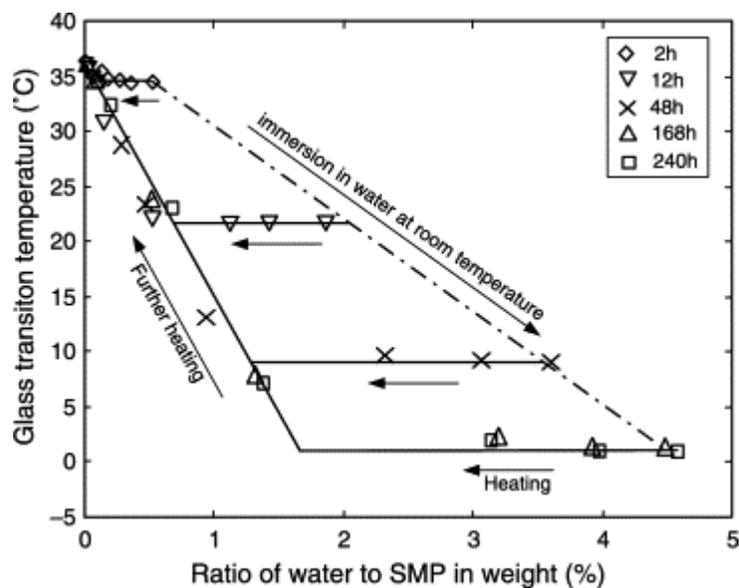


Fig. 5 Glass transition temperature vs. ratio of water to SMP in weight percent.

Effect of heating the polymers immersed in water .

A series of similar L- shaped curves are obtained when plotted for heating for different samples for which the immersion time are different .The evolution of the glass transition temperature upon heating can be divided in to two stages . In the first stage the transition temperature is kept almost constant, despite the continuous reduction of the water content. This corresponds to the removal of the free water .This shows that the free water has negligible effect on the glass transition temperature and it is fully recovered at relatively lower temperatures. In the second stage, the glass transition temperature starts to increase linearly with further decrease in the water content. This is due to the removal of the bound water molecules. With the complete evaporation of the water molecules the interaction between water and polymer vanishes and the hydrogen bond between N-H and C=O gradually reverts to its original state . So the shape memory polymer finally recovers its glass transition temperature.

8. Ways of activating Shape memory Polymer

(a) Thermo responsive shape memory polymers:

The shape memory polymers which change in shape with the change of temperature are called thermo responsive shape memory polymers. By far these are the most common shape memory polymers.

(b) Electrical heating induced shape memory effect:

The shape memory polymers are generally not conducting. So they are made Conductive by blending with carbon nano powders. The electric current is converted into heat . They recover the original shape when electric current is passed through the shape memory polymers.

(c) Light induced shape memory polymers:

The shape memory polymers which are to be activated by light should have some photo sensitive groups which act as molecular switches. The shape memory polymers are stretched and illuminated by a light of wavelength greater than a fixed wavelength and the photo sensitive groups form cross links .The polymer is locked in the new shape and retains the temporary shape even when the stress is released. When this is illuminated by a light of lower frequency, the cross linking cleaves allowing the material to go back to its original state.

(d) Magnetically induced shape memory effect

Non contact triggering of shape changes in polymers has been realized by incorporating magnetic nanoparticles in shape memory polymers and inductive heating of these compounds in alternating magnetic fields. Magnetic nanoparticles having an iron (III)oxide core in silica matrix could be incorporated in the shape-memory polymers.

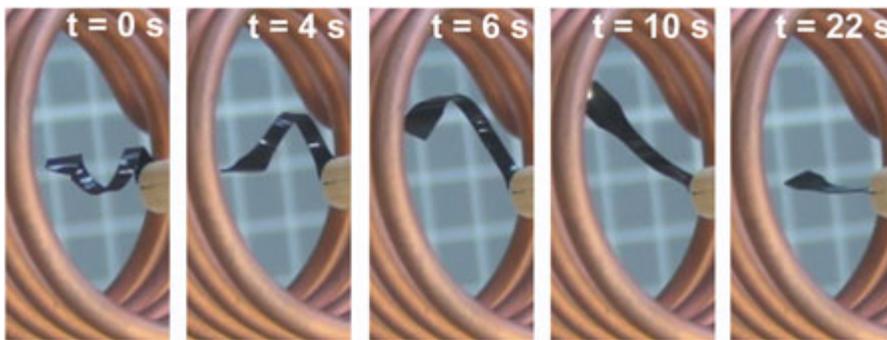


Fig 6. Sequence of photographs showing the shape-memory polymer (black strip) changing to its permanent shape in the presence of an alternating magnetic field.

(e) Water activated shape memory effect:

The Actuation of the polymer can be achieved by immersion in water :

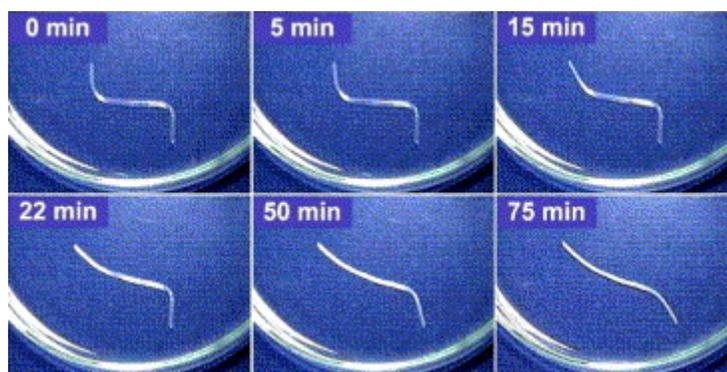


Fig.7 Recovery of functionally gradient SMP actuated by water in a sequence

A shape memory polymer which has the permanent shape of a straight rod is programmed into a Z shape . The left part of the polymer is dipped into water and the right part is not dipped . There is a reduction of the glass transition temperature for the left part and it gets actuated ie gets back to its original form with the help of the room temperature water itself .

9. A General Thermo mechanical cycle :

The typical thermo mechanical cycle for shape memory polymers would consist of the following four steps :

- 1) Deform the polymer at a temperature greater than the glass transition temperature(T_g)
- 2) Fix the deformed sample and cool it below the glass transition temperature (T_g)
- 3) Release the constraint .
- 4) Heat the sample above the transition temperature to get back the original shape .

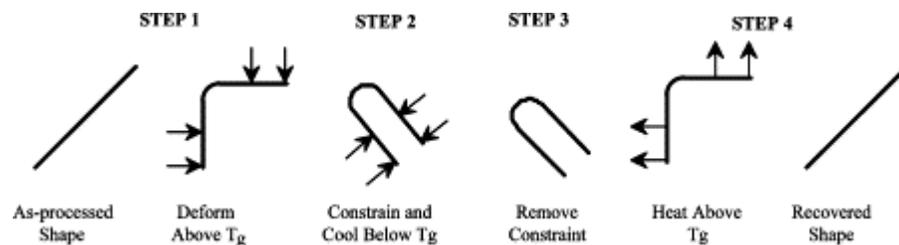


Fig 8 Schematic of the idealized thermo-mechanical cycle leading to unconstrained strain recovery for a shape memory polymer.

The polymer must first be processed (molded and cured) to the desired shape. In Step 1 , the as-processed material is deformed at a temperature above T_g , In Step 2, the polymer is held in its final deformed shape and cooled below T_g typically to a temperature near room temperature. Removal of the constraint required to bend the polymer at the higher temperature is performed in Step 3. Generally, the polymer can hold the deformed shape in Step 3 indefinitely, until recovery is necessary. In Step 4, the polymer is heated above T_g to recover the original undeformed as-processed shape. If partial constraint remains on the SMP in Step 3, then full strain recovery will not occur, but rather the material will generate a counteracting force.

10. Quantification of the shape memory properties:

The shape-memory properties can be quantified using the various strain values obtained in the cyclic experiment. Equation below defines the strain recovery rate (RT) as a measure of how much of the strain, which has been applied in the programming stage, is recovered during the shape-memory transition from one cycle to the next

$$R_r(N) = \frac{\epsilon_m - \epsilon_p(N)}{\epsilon_m - \epsilon_p(N-1)} \quad \text{Eq ...2}$$

where N is the cycle number, ϵ_m is the maximum strain imposed on the material. $\epsilon_p(N)$ and $\epsilon_p(N-1)$ are the strains of the sample in two successively passed cycles in the stress-free state before yield stress is applied.

The percentage strain recovery is the amount of the applied strain that is recovered in the same cycle following heating above TS

$$\% \text{ Strain recovery} = \frac{\epsilon_m - \epsilon_p}{\epsilon_m} \times 100\% \quad \text{Eq ...3}$$

ϵ_m is the maximum strain imposed on the material. ϵ_p is the strain in the sample at the end of same cycle before yield stress is applied.

The percentage strain fixity quantifies the ability of the switching segment to hold the shape after the sample has been stretched.

$$\% \text{ Strain fixity} = \frac{\epsilon_s}{\epsilon_m} \times 100\% \quad \text{Eq...4}$$

10. Modelling of Shape memory polymers:

The Constitutive model facilitate the prediction of recoverable stress and strain levels under varying degrees of constraint, as will be invariably experienced in SMP applications.

For temperatures less than the glass transition temperature (T_g), the large-scale conformational changes are not possible but localized conformational motions are allowed. At temperatures well below T_g , the polymer is in a “glassy” state and behaves as an elastic solid at small strains. The low temperature elasticity is due to primary bond stretching, which causes a change in internal energy

For temperatures above T_g , the polymer is in a “rubbery” state. The stiffness of the polymer is low, and the deformation energy is converted into a free conformational entropy change. In the rubbery state, the elastic deformation of an ideal network polymer produces a change in the conformational entropic state of the polymer chains, and the interaction between chain molecules is relatively neglectable. In both the glassy and rubbery states, the elastic strain can be stored “instantaneously” and released “instantaneously” upon removal of the applied stress.

The entropic state induced by the high temperature deformation can be stored “temporarily” at low temperatures, i.e. “frozen,” by emerging atomic interactions, which is defined as the internal stress field. The frozen strain can only be released when strong molecular interaction has disappeared after subsequent heating to a high temperature. The driving force for the strain release is micro-Brownian thermal motion, which becomes increasingly important at higher temperature. The theory of rubber elasticity is reasonable up to relatively large elongations as long as the cross-link density is moderate. In the rubbery state, the Young’s modulus predicted by rubber elasticity theory is proportional to the absolute temperature and the cross-linking density.

The polymer chains between the cross-linking nodes can be considered as entropy springs, which implies that the polymer chains accommodate conformational rotation around C–C bonds. In the rubbery state, when subjected to deformation, the entropy of the polymer will decrease. With a decrease of temperature and free-volume, the free conformational rotation of an individual C–C bond will gradually transform into cooperative conformational rotation with its neighbors . The number of polymer chain segments involved in the cooperative conformational rotation will increase with the decrease of the temperature for $T < T_g$ and the large-scale entropic changes will be prevented, and only the localized entropic motions will occur in the polymer when a load is applied. Two kinds of C-C bonds co-exist in the polymer namely: a) Frozen

bonds and b) Active bonds. The frozen bond represents the fraction of the C–C bonds that is fully disabled with regard to the conformational motion, while the active bond represents the rest of the C–C bonds that can undergo localized free conformational motions. Frozen bonds are predominant when cooled to the glassy state,

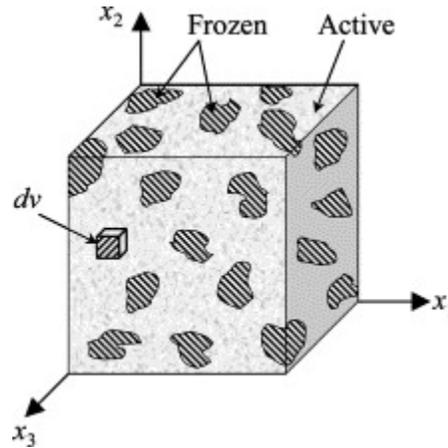


Fig. 9. Schematic diagram of the 3-D shape memory polymer constitutive model. Existence of two extreme phases in the polymer is assumed. The diagram represents a polymer in the glass transition state with a predominant active phase.

At an arbitrary temperature during the thermomechanical cycle, we assume that the polymer is a mixture of two kinds of extreme phases: the “frozen phase” (dark shaded region) and the “active phase” (light shaded region). The frozen phase (hard phase), is composed of the frozen bonds. In this phase, the conformational rotation corresponding to the high temperature entropic deformation is completely locked (stored), while the internal energy change such as the stretching or small rotation of the polymer bonds can occur. In addition, any further conformational motion of the material is impossible in the frozen phase. The frozen phase is the major phase of a polymer in the glassy state at low temperature. In contrast, the active phase (soft phase) consists of the active bonds, so the free conformational motion can potentially occur and the polymer exists in the full rubbery state

the “frozen fraction” (frozen volume fraction) and the “active fraction” (active volume fraction) are defined as:

$$\phi_f = \frac{V_{fm}}{V}, \quad \phi_a = \frac{V_{as}}{V}, \quad \phi_f + \phi_a = 1, \quad \text{Eq. . . 5}$$

Where V is the total volume of the polymer, V_{frz} is the volume of the frozen phase and V_{act} is the volume of the active phase.

the frozen and active volumes account for the overall volume of the material, including the free-volume and the volume occupied by the polymer chains.

we assume that under the boundary condition of a sufficiently slow strain rate and the thermal condition of a slow constant heating/cooling rate, ϕ_f and V_{frz} are dependent only on temperature T :

$$\phi_f = \phi_f(T), \quad V_{\text{frz}} = V_{\text{frz}}(T). \quad \text{Eq. . .6}$$

At certain temperatures, entropic changes can be frozen and stored “temporarily” after unloading; therefore, if the material has been strained at a high temperature, $\phi_f(T)$ captures the fraction of strain storage as a function of temperature.

When a stress of σ is applied, let the strain induced is ϵ . The stress applied would be the same for both the phases. But the total strain is sum of the strains in both the phases :

$$\text{Total strain } \epsilon = \phi_f \epsilon_f + (1 - \phi_f) \epsilon_a \quad \text{Eq. . .7}$$

where ϵ_f is the strain in the frozen phase and ϵ_a is the strain in the active phase.

In the frozen phase, the entropic portion of the pre-deformation is assumed to be completely locked and stored during cooling. Due to the localized freezing process, the entropic frozen strain, ϵ_f^e can be anisotropic inside the ever-growing frozen phase and should be considered as a function of the position vector, \mathbf{x} . An integral over the frozen fraction volume should be used to sum the local contribution of ϵ_f^e . From the model, the deformation of the frozen phase arises from three parts: the average of the frozen (stored) entropic strain, the internal energetic strain ϵ_f^i and the thermal strain ϵ_f^T :

$$\epsilon_f = \frac{1}{V_{\text{frz}}} \int_0^{V_{\text{frz}}} \epsilon_f^e(\mathbf{x}) dV + \epsilon_f^i + \epsilon_f^T. \quad \text{Eq. . . .8}$$

In the active phase, the deformation is composed of two parts: the external stress-induced entropic strains ϵ_a^e and the thermal strain ϵ_a^T :

$$\boldsymbol{\varepsilon}_s = \boldsymbol{\varepsilon}_s^e + \boldsymbol{\varepsilon}_s^T, \quad \text{Eq. 9}$$

Therefore the total strain $\boldsymbol{\varepsilon}$ is got by substituting Eq. 8 and Eq. 9 in Eq. 7.

$$\boldsymbol{\varepsilon} = \left(\frac{1}{V} \int_0^{V_m} \boldsymbol{\varepsilon}_i^e(\mathbf{x}) dV \right) + (\phi_f \boldsymbol{\varepsilon}_f^e + (1 - \phi_f) \boldsymbol{\varepsilon}_s^e) + (\phi_f \boldsymbol{\varepsilon}_f^T + (1 - \phi_f) \boldsymbol{\varepsilon}_s^T). \quad \text{Eq. 10}$$

we define the first bracketed term on the right-hand side of the above Equation to be the “stored strain,” $\boldsymbol{\varepsilon}_s$, which reflects the strain storage as a function of temperature and is often called a “history” variable. Letting

$$d\phi = \frac{dV}{V} \quad \text{Eq. 11}$$

represent a small volume fraction around the position \mathbf{x} , the internal variables $\boldsymbol{\varepsilon}_i^e$ and ϕ_f can be incorporated into the evolution of this new internal variable $\boldsymbol{\varepsilon}_s$ in a cooling or heating process:

$$\boldsymbol{\varepsilon}_s = \frac{1}{V} \int_0^{V_m} \boldsymbol{\varepsilon}_i^e(\mathbf{x}) dV = \int_0^{V_m} \boldsymbol{\varepsilon}_i^e(\mathbf{x}) \frac{dV}{V} = \int_0^{\phi_f} \boldsymbol{\varepsilon}_i^e(\mathbf{x}) d\phi. \quad \text{Eq. 12}$$

$\boldsymbol{\varepsilon}_f^e$ and $\boldsymbol{\varepsilon}_s^e$ are elastic strains.

The glassy state yield behavior is not considered and the non-linearity of rubbery elasticity can be ignored for small strains, we assume that the material behaves in a linear elastic manner in both the frozen and active phases. Thus, the internal variables, $\boldsymbol{\varepsilon}_f^e$ and $\boldsymbol{\varepsilon}_s^e$, can be related to the stress tensor through the Generalized Hooke’s laws:

$$\boldsymbol{\varepsilon}_f^e = \mathbf{S}_i : \boldsymbol{\sigma}, \quad \boldsymbol{\varepsilon}_s^e = \mathbf{S}_e : \boldsymbol{\sigma}, \quad \text{Eq. 13}$$

where \mathbf{S}_i is the elastic compliance fourth-order tensor corresponding to the internal energetic deformation, while \mathbf{S}_e is the elastic compliance fourth-order tensor corresponding to the entropic deformation. Here, we define the second additive term on the right-hand side of Eq. 10 to be the mechanical (elastic) strain $\boldsymbol{\varepsilon}_m$:

$$\boldsymbol{\varepsilon}_m = \phi_f \boldsymbol{\varepsilon}_f^e + (1 - \phi_f) \boldsymbol{\varepsilon}_s^e = (\phi_f \mathbf{S}_i + (1 - \phi_f) \mathbf{S}_e) : \boldsymbol{\sigma}. \quad \text{Eq. 14}$$

The total thermal strain ε_T defined by the third part of Eq...10 and can be expressed in terms of thermal expansion coefficient ' α ' of the equivalent homogeneous material,

$$\begin{aligned}\varepsilon_T &= \phi_f \varepsilon_f^T + (1 - \phi_f) \varepsilon_a^T = \left(\int_{T_0}^T \phi_f \alpha_f(\theta) d\theta + \int_{T_0}^T (1 - \phi_f) \alpha_a(\theta) d\theta \right) \mathbf{I} = \left(\int_{T_0}^T \alpha(\theta) d\theta \right) \mathbf{I}, \\ \alpha &= \phi_f \alpha_f + (1 - \phi_f) \alpha_a,\end{aligned}\quad \text{Eq...15}$$

where α_f and α_a are the thermal expansion coefficients of the frozen phase and the active phase, respectively, and \mathbf{I} is the identity tensor. Therefore the total strain is

$$\varepsilon = \varepsilon_s + \varepsilon_m + \varepsilon_T. \quad \text{Eq...16}$$

Therefore the overall constitutive equation for the polymer in a thermomechanical cycle:

$$\sigma = (\phi_f \mathbf{S}_i + (1 - \phi_f) \mathbf{S}_e)^{-1} : (\varepsilon - \varepsilon_s - \varepsilon_T) \quad \text{Eq...17}$$

the entropic strain $\varepsilon_s^e(T)$ in the active phase is governed by the Hooke's law

During cooling with a change of temperature dT , a fraction of the active material $d\phi$ at $\mathbf{x}(T)$ will be frozen and transform into a new fraction of the frozen material. As a result, the current active entropic strain $\varepsilon_s^e(\mathbf{x}(T))$ is fixed as the stored strain $\varepsilon_s^e(\mathbf{x})$. Thus we have drawn a relation between the position vector and the temperature history in the sense that the frozen strain at position \mathbf{x} is converted from the active strain at temperature T . Consequently we deduce that:

$$\varepsilon_s^e(\mathbf{x}) = \varepsilon_s^e(\mathbf{x}(T)) = \varepsilon_s^e(T) = \mathbf{S}_e(T) : \sigma(T). \quad \text{Eq..18}$$

With the definition of ε_s in Eq..12 and the constitutive relationship in Eq.17, we have the temperature derivative of the stored strain as a function of temperature:

$$\begin{aligned} \frac{d\varepsilon_s}{dT} &= \varepsilon'_s(x) \frac{d\phi_r}{dT} = S_e(T) : \sigma(T) \frac{d\phi_r}{dT} \\ &= S_e(T) : (\phi_r S_i + (1 - \phi_r) S_e)^{-1} : (s - \varepsilon_s - \varepsilon_r) \frac{d\phi_r}{dT}. \end{aligned} \quad \text{Eq..19}$$

The Young's modulus E of the polymer is given as:

$$E = \frac{1}{\frac{\phi_r}{E_i} + \frac{1 - \phi_r}{E_e}}, \quad \text{Eq...20}$$

where E_i is the modulus corresponding to the internal energetic deformation and E_e the modulus corresponding to the entropic deformation. We assume E_i is a constant in the temperature range considered.

From the rubbery elasticity of a network polymer, E_e is a linear function of absolute temperature and becomes zero at 0 K. So we have:

$$E_i = \text{constant}, \quad E_e = 3NkT, \quad \text{Eq...21}$$

Reducing it to a one dimensional case, the 1-D small-strain constitutive equations and material property functions of the shape memory polymer model are:

$$\text{Constitutive equation : } \sigma = \frac{s - \varepsilon_s - \int_{T_h}^T \alpha dT}{\frac{\phi_r}{E_i} + \frac{1 - \phi_r}{E_e}} = E \left(s - \varepsilon_s - \int_{T_h}^T \alpha dT \right), \quad \text{Eq...22}$$

$$\text{Temperature derivative of stored strain : } \frac{d\varepsilon_s}{dT} = \frac{s - \varepsilon_s - \int_{T_h}^T \alpha dT}{E_e \left(\frac{\phi_r}{E_i} + \frac{1 - \phi_r}{E_e} \right)} \left(\frac{d\phi_r}{dT} \right). \quad \text{Eq...23}$$

Young's modulus:

$$E = \frac{1}{\frac{\phi_r}{E_i} + \frac{1 - \phi_r}{E_e}}, \quad \text{Eq...24}$$

Modulus of the internal energetic deformation: $E_i = \text{constant}$ Eq.....25

Modulus of the entropic deformation: $E_e = 3NKT$ Eq....26

Coefficient of thermal expansion: $\alpha = \frac{1}{L} \frac{dL}{dT}$

Subsequently, the uniaxial stress evolution of the shape memory polymer under various thermomechanical conditions can be predicted.

11. Draw backs of shape memory polymers:

A significant draw back of shape memory polymer is because of the relatively low stiffness values. A low stiffness value indicates a relatively small value of the recovery force under constraint. But adding reinforcements help in overcoming the drawbacks . They allow us to tailor the material stiffness. Fiberglass and Kevlar reinforcements increased the stiffness of the SMP resins and reduced recoverable strain levels. Moreover, discontinuous fiber reinforced composites showed shape recovery in all directions, while continuous fiber reinforced composites only showed recoverability under transverse tension or bending.

The addition of nanoparticulate SiC reinforcements increases both the hardness and elastic modulus of the base resin material. The increase in both of these material properties is a direct consequence of the relatively high hardness/modulus of the SiC particles relative to the polymer matrix. The hardness and modulus increases are directly proportional to the weight fraction of SiC. The hardness and modulus of the composite material can be tailored for a given application by altering the weight fraction of the SiC, or using alternative reinforcement materials/architectures.

12. Applications :

a) Intracranial aneurysm:

Intracranial aneurysm effect between 2 % to 6% of the world population .It is a very serious problem which goes undetected until the aneurysm ruptures , causing hemorrhaging within the sub arachnoid space surrounding the brain .The typical treatment is by embolization of platinum coils .

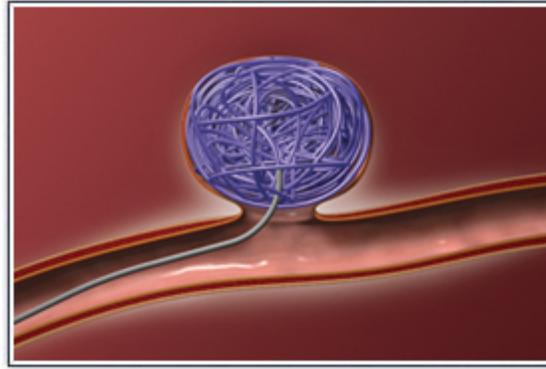


Fig 10. aneurysm with the platinum coils introduced.

In this process , a large number of coils were introduced into the aneurysm to occlude the flow of blood. The blood becomes stagnant in this area and this leads to clotting of blood. This leads to thrombus formation .The desirable effect could be got if there is a thick interconnected matrix of thrombus and scar tissue formed at the neck of the aneurysm .

Re-canalization problem occurs if there is a limited fibrous scar tissue ,unorganized thrombus and undeveloped neo-intima covering the neck of the aneurysm.In case of platinum, since it is bio-inert , the endothelial adhesion on the surface is limited. If a stable matrix is not formed at the neck of the aneurysm , the thrombus re-opens and blood flow is re-established .This corresponds to about 15 % of the cases. so one solution would be to use the coils which are bio-active . Polyurethane coated platinum coils were found to give advantages over the normal coils .

But greater benefits were observed when shape memory polymers were used . The shape memory polymer due to its shape memory effect has a shape pre-determined. So, it can be designed to take a shape which would be comfortable while introducing it into the body .when inside the aneurysm because of the temperature it can retrieve the desired shape .For example a helix shape was fixed to be the permanent shape so that it can occlude effectively .And because the shape memory polymers introduced were bio-active ,a stable matrix was formed at the neck of the aneurysm and unlike the case of platinum foils the recanalization problem do not occur .

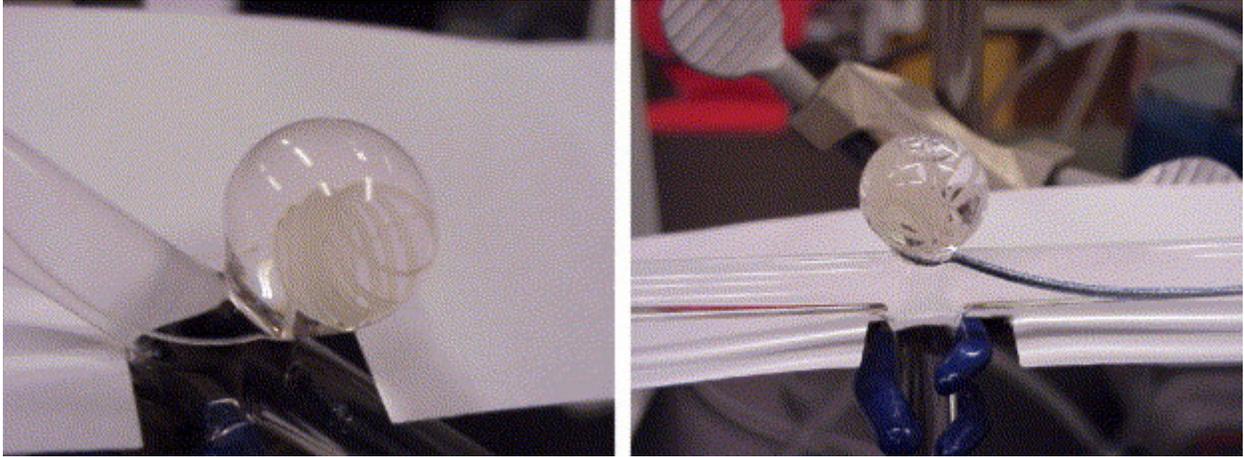


Fig. 11. Deployment of two SMP coils under simulated flow conditions. Their helix shape was completely retrieved as shown in the right side figure.

b) In the Mechanical Removal of clots :

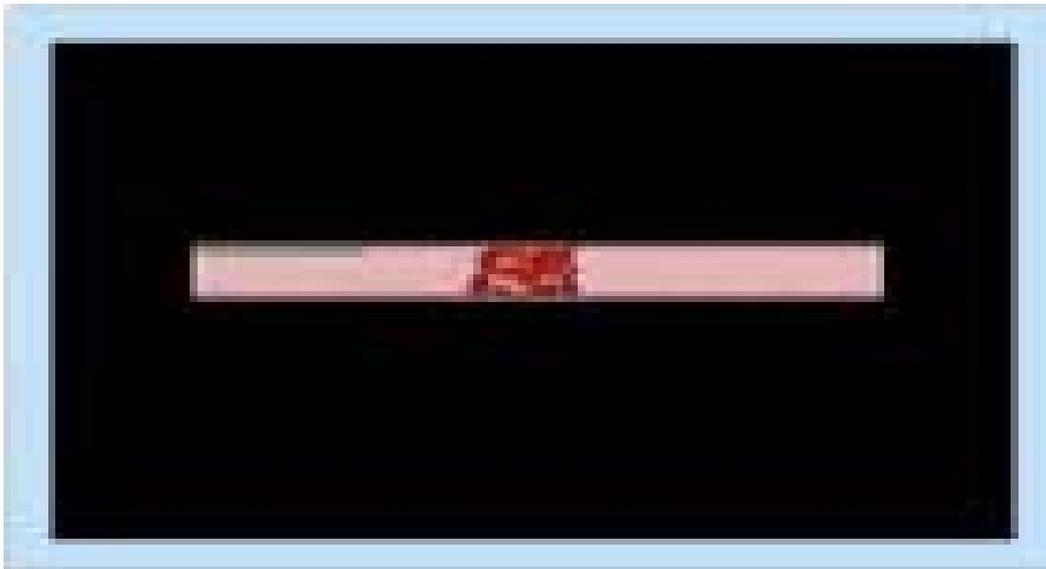


Fig. 12 The shape memory polymer in the form of rod being introduced into the blood vessel containing the clot .

Shape memory polymers can be used in the removal of clots . The shape memory polymer is introduced into a vessel in the form of a straight rod.(as shown in Fig 13(a)) This is the secondary shape fixed .The primary shape is a tapered cork screw shape(Fig 13(b)). After it passes through the clot , the shape memory polymer is activated using a laser and it get backs its primary cork screw shape and hold

the clot fixedly .Both of them are then removed . so the blood flow is retained again in the blood vessel.

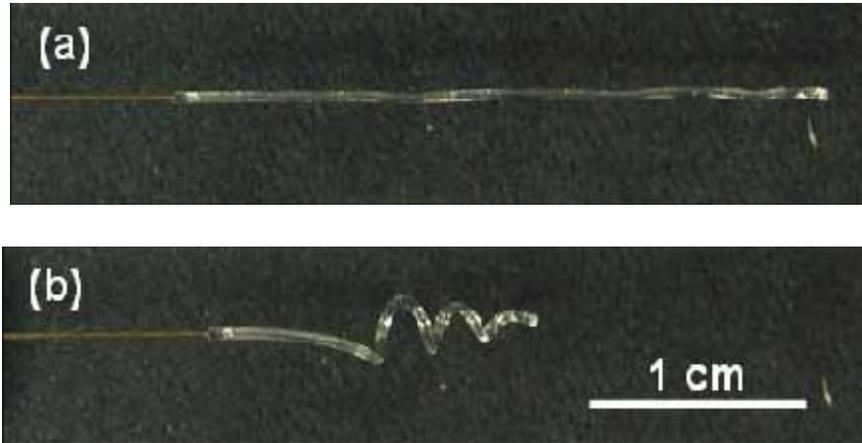


Fig. 13. SMP in its (a) secondary straight rod and (b) primary corkscrew forms.

c)For self-Tightening sutures :

Shape memory polymers are very useful as self –tightening sutures . In general the sutures are to be stitched very carefully . They may damage the cells of the skin if the threads are stitched very tight .on the other hand , if the threads are too loose , it does not do the required function .The shape memory polymers if used , the threads can stitched loosely and when the threads come into contact with the body , because of the body temperature , it contracts to tighten it to the just required force .

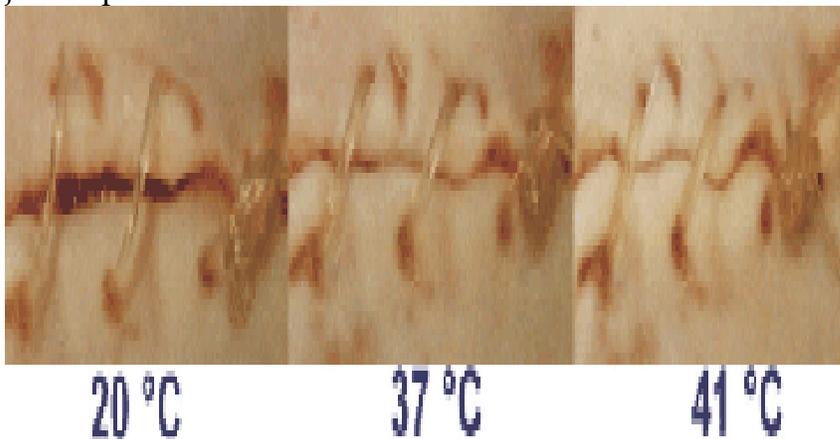


Fig 14 . the suture are getting tightened as the temperature reaches the body temperature.

d) Applications in breathable textiles :

A higher comfort level can be achieved using shape memory polymer coated garments. By coating with shape memory polymers like shape memory poly urethanes, we can control the permeability to a large extent . we can have a high water vapour permeability at a higher temperature and a lower water vapour permeability at a lower temperature, thus making it useful to be used in both the conditions .This allows it to be used for breathable textiles.

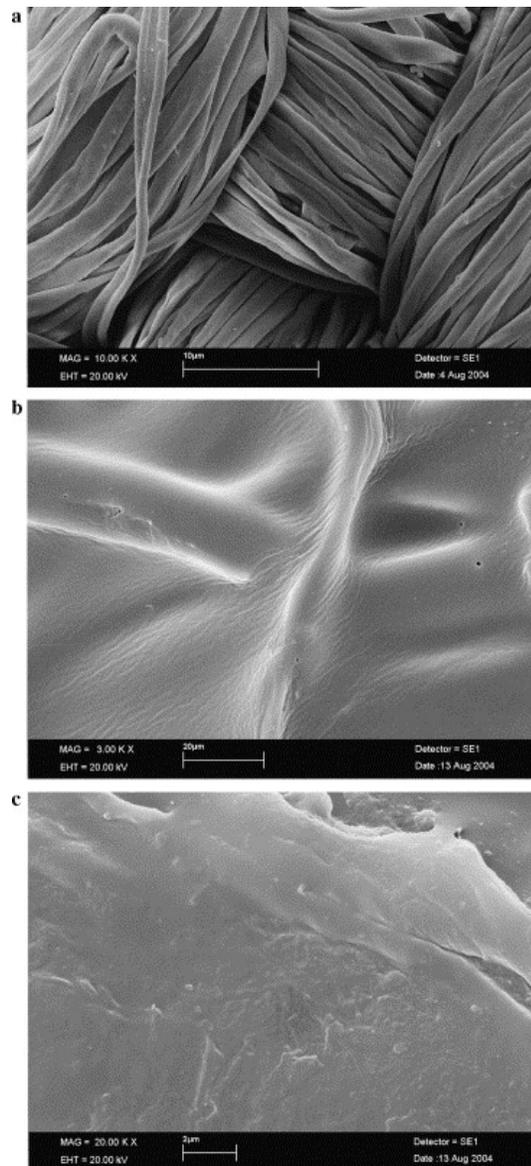


Fig. 15.. SEM image of (a) uncoated fabric, (b) and (c) fibres coated with different shape memory polymers .The uncoated fibre is porous. the coated fibres have a non-porous layer on it

Mechanism for the coated fibres :

The polymer forms a thin layer of non-porous surface on the fibres .so the water vapour permeability would be a three step mechanism of sorption-diffusion-desorption mechanism . The water vapour molecules would be absorbed onto the polymer surface and then the diffusion takes place , finally the water molecules are desorbed out of the surface because of the concentration differences with the environment .

At the crystal melting point of the soft phase , the micro -brownian motion of the soft phase would occur . This leads to discontinuous changes in the density and provide enough gaps for the water vapour molecules to pass through .

General observations :

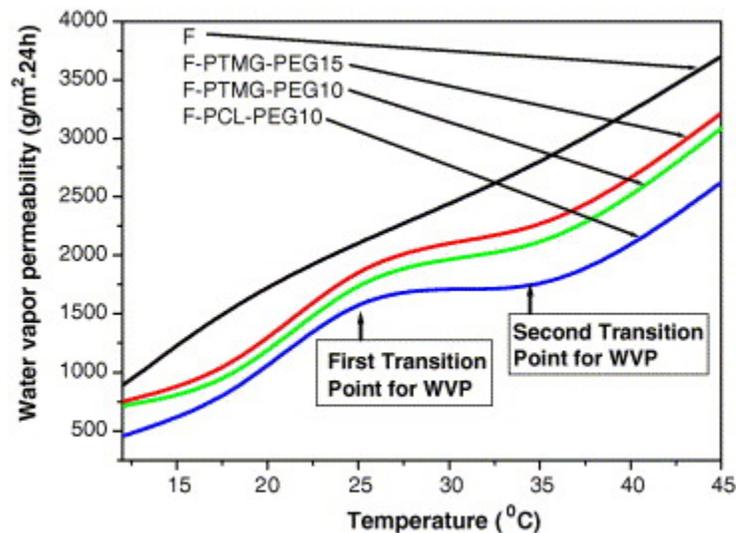


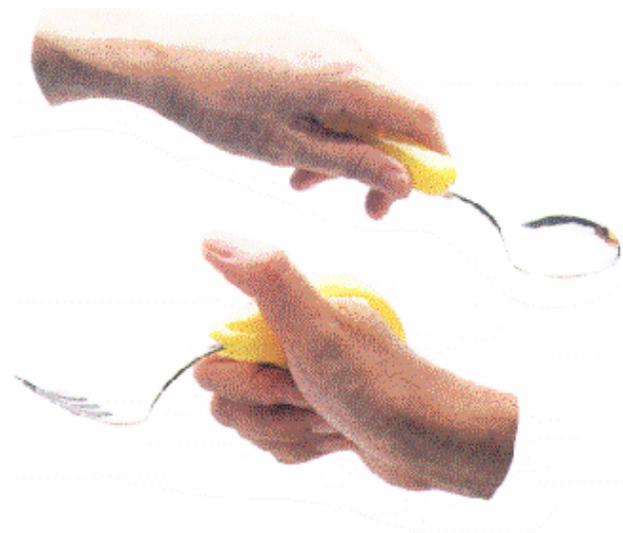
Fig. 16. Water vapor permeability of SMPU coated fabrics.

- 1) The water vapour permeability of uncoated fabric increases linearly with the increase in temperature .
- 2) The water vapour permeability suddenly increases at the phase transition of the soft segment phase .
- 3) The increase in the hydrophilic segment content in the shape memory increases the water vapour permeability .

- 4) A decrease in the water vapour permeability would occur if groups which increase the inter-chain interaction such as ester groups are present

e) Boon for the disabled:

Shape memory polymers can be used to make handles of spoons. These spoons can simply be put in hot water and the required deformation is given to impart a required shape needed. It is then put in cold water and the shape is fixed. This can now be put to use for the disabled person. The original shape is got back by just heating it in boiling water. This provides a flexibility to adjust any kind of shape needed.



(c) Spoon and fork handles for handicapped.

Fig 17.

f) Active Disassembly:

Screws of the components can be made of shape memory polymers. When sent to recycling, these screws come out by themselves when the condition of temperature is provided. The hooks are even made of these polymers and so when the temperature is provided they unhook and push each the pieces away from each other. So in this way all parts are easily separated. This

method allows for savings of time, labour and money and even the recycling is better.

13) Ongoing research:

Presently we have shape memory polymers which can remember one shape. Now people are trying to develop the shape memory polymers which can remember more than position. The polymer can shift between two positions. This could lead to artificial muscle.

References :

1) *Materials Science and Engineering: C, Volume 26, Issue 8, September 2006, Pages 1373-1379*

Janet M. Hampikian, Brian C. Heaton, Frank C. Tong, Zhuqing Zhang and C.P. Wong

2) *Carbohydrate Polymers, In Press Corrected Proof, Available online 22 August 2006,*

S. Mondal and J.L. Hu

3) *Biomaterials, Volume 27, Issue 24, August 2006, Pages 4288-4295*

Xiaotong Zheng, Shaobing Zhou, Xiaohong Li and Jie Weng

4) *Polymer, Volume 47, Issue 4, 8 February 2006, Pages 1348-1356*

B. Yang, W.M. Huang, C. Li and L. Li

5) *International Journal of Plasticity, Volume 22, Issue 2, February 2006, Pages 279-313*

Yiping Liu, Ken Gall, Martin L. Dunn, Alan R. Greenberg and Julie Diani

6) *Materials Today, Volume 8, Issue 6, June 2005, Page 15*

John K. Borchardt

7) *European Polymer Journal, Volume 41, Issue 5, May 2005, Pages 1123-1128*

Bin Yang, Wei Min Huang, Chuan Li and Jun Hoe Chor

8) *Mechanics of Materials, Volume 36, Issue 10, October 2004, Pages 929-940*

Yiping Liu, Ken Gall, Martin L. Dunn and Patrick McCluskey

- 9) *Biomaterials*, Volume 24, Issue 3, February 2003, Pages 491-497
Annick Metcalfe, Anne-Cécile Desfaits, Igor Salazkin, L'Hocine Yahia, Witold M. Sokolowski and Jean Raymond
- 10) *Mechanics of Materials*, Volume 33, Issue 10, October 2001, Pages 545-554
Hisaaki Tobushi, Kayo Okumura, Shunichi Hayashi and Norimitsu Ito
- 11) *Mechatronics*, Volume 10, Issues 4-5, 1 June 2000, Pages 489-498
G. J. Monkman
- 12) *e 2*, 15 September 1994, Pages 253-263
R. P. Kusy and J. Q. Whitley
- 13) *Thermomechanical properties in a thin film of shape memory polymer of polyurethane series*, *smart Mater,struct* 5(1996)483-491. Hisaaki Tobushi, Hisashi Haray, Etsuko Yamada and Shunichi Hayashi.
- 14) *Laser-activated shape memory polymer intravascular thrombectomy device*, *optical society of America*, 2005. Ward Small IV¹, Thomas S. Wilson¹, William J. Bennett², Jeffrey M. Loge², and Duncan J. Maitland