Degradation behavior of shape memory polymer due to water and diesel fuel

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DEGRADATION BEHAVIOR OF SHAPE MEMORY POLYMER DUE TO WATER AND DIESEL FUEL

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by
Mohammad Nazmul Hasan Nahid
B.Sc., Bangladesh University of Engineering and Technology, 2007
August 2010
ACKNOWLEDGEMENT

I would like to thank my advisor, Dr. Muhammad A. Wahab. The works presented in this thesis are not possible without his support and guidance over the last two years. I would also like to thank my co-advisor Dr. Kun Lian for his invaluable help and feedbacks during the research. I would also like to thank NASA-EPSCoR for their financial support.

I would like to express my gratitude to my committee member, Dr. Guoqiang Li for his invaluable comments and probing questions. I would like to thank the many professors who have taught me at Louisiana State University. Also I would like to thank Prof. Donghui Zhang of Chemistry for her assistance in the use of FTIR facility in the Department of Chemistry at Louisiana State University (LSU).

I am most grateful to my family members for their continuous support and encouragement throughout my research period at LSU. I thank my parents for their understanding and support in my decision to come to the United States and pursue graduate studies at LSU.
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NOMENCLATURE

ω  Frequency (rad/s)

ε  Strain (mm/mm)

σ  Tensile Stress (N/m$^2$, Pa)

η  Viscosity (Pa-s)

ε$_m$  Total Deformation (mm)

ε$_p$  Unrecovered Plastic Deformation (mm)

ε$_u$  Elastic Deformation (mm)

E  Young’s Modulus or Modulus of Elasticity (N/m$^2$, Pa)

E”  Loss Modulus (N/m$^2$, Pa)

E’  Storage Modulus (N/m$^2$, Pa)

E*  Complex Modulus (N/m$^2$, Pa)

\tan{\delta}  tangent delta (measure of damping capacity of the material) =

\frac{E”}{E’} = \text{ratio of Loss modulus to Storage modulus}

i  Complex Number

K  Boltzmann Constant ($1.3806503\times10^{-23}$ m$^2$kg $s^{-2}\circ K^{-1}$)

R_f  Shape Fixity
R_r  Shape Recovery

S   Entropy

T_g  Glass Transition Temperature (°C)

T_{gh}  Glass Transition Temperature of hard segment (°C)

T_{gs}  Glass Transition Temperature of soft segment (°C)

T_m  Melting Transition Temperature (°C)

V_r  Shape Recovery Speed (m/s)

W   Probability
Shape memory polymers (SMP) are smart materials, which have the ability to memorize the original shape or permanent shape. When energy is supplied to the temporary deformed shape of SMP, mainly in the form of heat, it goes back to its original or permanent shape. Owing to these characteristics shape memory polymers can be used as a sensor, an actuator, a transplant, as well as structural materials in wide range of applications.

Due to its shape memory capability, the amount of research and its application in various fields have increased at a faster rate over the last two decades. One of the most striking features of SMP is its ability to produce recovery force. In this thesis, the recovery force produced by Veriflex- SMP has been identified and measured. On the other hand, despite its importance and the number of experiments that have been carried out in earlier researches, its degradation behavior is still not completely known; and only a limited amount of work have been reported in the literature. In this thesis, the experiments have been carried out to evaluate the degradation behavior of Veriflex- SMP (industry supplied SMP samples) upon exposure to two different types of liquids; water and diesel fuel separately. The SMP samples are subjected to a continuous degradation process by immersing in the liquids for up to 3 months.

In the process of this study, the changes in properties of SMPs due to the degradation process are investigated through dynamic mechanical analysis. The percentages of water and diesel uptake are also measured and Fourier Transform infrared (FTIR) spectra are determined to investigate the change at molecular level.

It has been found that the “glass transition temperature, $T_g$” decreases due to immersion in water and diesel fuel. The immersion of Veriflex- SMP in water and diesel fuel facilitates the
breakage of existing bonds and the formation of new bonds, thereby increasing the mobility of polymeric chains. In addition, water and diesel fuel are found to be effectively plasticize the SMPs, by reducing the storage modulus; and thus decreasing the structural integrity of the SMP.

It is also observed that upon exposure to diesel fuel for a couple of weeks, (i.e., duration of 2- weeks only) the glass transition temperature, $T_g$ of Veriflex- SMP goes below the room temperature. As a result, the styrene based Veriflex- SMP goes back to the original shape from the deformed shape without the application of external energy or stimuli.

The stress relaxation tests (stress-controlled test) are also conducted to determine the changes in physical properties of SMP. The decay in stress level is monitored due to the degradation by water and diesel fuel separately. The decay of the stress is found much faster and eventually to a much lower value in the degraded samples, in comparison to the untreated samples, tested under the similar conditions. It is also found that the stress decay is increased with the increase of immersion time in water and in the diesel fuel. From Fourier Transform Infrared (FTIR) tests it has been found that the formation of hydrogen bonding between the SMP and the solvents (water and diesel fuel) is the main reason for the degradation of SMP; although the hydrogen has a minor effect on the structure of SMP, but it has an obvious influence on the glass transition temperature, $T_g$. 
1. INTRODUCTION

In the last two decades, there has been increased interest in Shape Memory Polymer (SMP). Like other polymers, the structural and physical property of SMP changes due to degradation and ageing. This time-dependent behavior and degradation is the result of the non-equilibrium nature of the glassy-state, which corresponds to an absence of long-range motion of chains. The importance of this phenomenon in practical applications arises from the simple fact that the performance of SMP must be predictable to ensure compatibility with design requirement throughout the anticipated service life of the polymer products. The degradation behavior of SMP is just as important as other factors, such as, temperature, from the viewpoint of the evaluation of SMP. Thus, the knowledge of the degradation behavior of SMP by various solvents is important for the efficient use of it.

Due to the capability of recovering the large deformation, the SMP belongs to a special group of smart material whose property can be altered in a controlled way.

1.1 Smart Material

Smart material is a special kind of material, which has the ability of sensing, processing, actuating, self-diagnosing, and self-recovering. They can sense the change in environment and act accordingly to minimize the action of the changes in environment; similar to a living creature that can sense, make decisions, and take actions. Their physical and chemical properties are sensitive to the change in environment such as pressure, temperature, electric field, pH level, magnetic field, and optical wavelength etc. They utilize their own properties and functions to achieve smart action such as capability of piezoelectric material to produce force upon the application of electric voltage. So far, several smart materials have been invented, notable ones are given below:
- **Piezoelectric Material**
  Piezoelectric material has the ability to produce electric voltage when subjected to force; conversely it will generate force when voltage applied on it.

- **Electro- rheological (ER) Fluid**
  These are suspension of fine particles in an electrically insulating fluid. The viscosity of this fluid changes significantly when an electric field is applied on it.

- **Magneto- rheological (MR) Fluid**
  These are suspension of very fine particles in a carrier fluid, namely oil. Like ER fluid, the viscosity of magnetorheological fluid increases when a magnetic field is applied on it. Ultimately, it becomes visco-elastic solid.

- **Shape Memory Material**
  This material has the ability to return from its temporary deformed shape to permanent shape upon the application of external stimulus such as heat. In one word, it remembers its original shape. Shape memory polymer is a type of shape memory material, which has been investigated in this research.

- **Optical Fiber**
  Optical fiber is a kind of glass or plastic fiber, which carries light. The main principle upon which fiber optic works is its total internal reflection that occurs when light waves traveling in one medium encounters another medium.

  Shape memory materials have recently gained concentrated attention both in educational, research, and industrial sectors because of its ability to memorize the permanent or original shape, and its wide-ranging prospects for future application in various fields.
1.2 Shape Memory Materials

Shape memory materials belong to a special class of smart materials that have the ability to remember their original shape. Shape memory materials are stimuli-responsive materials. For example, a temperature responsive shape memory material is the one that undergoes a structural change upon reaching a certain temperature, called the “transition temperature”, where the polymer goes from a brittle and glassy state to a flexible rubbery state. There are several classes of shape memory materials such as alloys [Srinivasan & Mcfarland, 2001], polymers [Andreas & Steffen, 2002], ceramics [Wei et al., 1998], and gels [Thierry et al., 2000]. Among these, Shape Memory Alloys (SMAs) and Shape Memory Polymers (SMPs) are widely used because of their desirable properties and varied applications.

1.2.1 Shape Memory Alloy (SMA)

Shape Memory Alloys are a class of shape memory material which undergoes solid to solid martensitic phase transformation upon the application of heat. SMAs have many advantages such as; they are strong and corrosion resistant. SMAs are used in a number of different fields, for example, vascular stents, orthodontic wires, vibration dampers, electrical connectors, and actuators [Thierry et al., 2000, Miao et al., 2002, Es-soumi et al., 2002]. But one of the most prominent drawbacks of SMA is its ability to recover only a very small amount of strain, (only up to approximately 15%) in comparison to Shape Memory Polymer (SMP) which has the ability to recover a very large amount of strain (usually >400%) [Hu, 2007].

1.2.2 Shape Memory Polymer (SMP)

Shape memory polymers are a special type of polymer, which can recover the permanent shape upon the application of external stimulus. The main advantage of shape memory polymer
is the ability of recovering a large amount of strain (usually >400%) in comparison to shape memory alloys (SMA) (up to 15%) and shape memory ceramics (2 - 3%) [Hu, 2007].

The material used in this research is Shape Memory Polymer due to its excellent shape recoverability. Before going into the details of the various topics of this thesis some of the basic features of SMP are discussed first.

1.2.2.1 Structure of Shape Memory Polymer

Generally, SMPs are phase-segregated linear block copolymers having (i) a “hard segment” and (ii) a “soft segment” in terms of molecular structure.

i. Hard Segment

Hard segments (or crystalline segments) are responsible for maintaining the permanent or original shape through intra or inter polymeric chain attractions such as hydrogen bonding or dipole-dipole interaction together with the physical or chemical cross-linking.

Figure 1: Network structure of SMP showing hard segments and soft segments
ii. **Soft Segment**

Soft segments (or amorphous segments) are responsible to freely absorb external stress by unfolding and extending their molecular chains.

In another word, shape memory polymers are typically elastic network equipped with external stimulus responsive switches. Temperature responsive shape memory polymers are the most notable ones because of their wide range of switching or transition temperature, which can easily be tailored by changing chemical composition. The transition temperature, upon which the polymer can be deformed into temporary shape or goes back to the original shape, of shape memory polymer can be of two types:

i. **Glass Transition Temperature, \( T_g \)**

The glass transition temperature of the material is the temperature, which is above the transition temperature of the soft or amorphous segment \( T_{gs} \) but below the transition temperature of the hard or crystalline segment \( T_{gh} \). In other words, at this transition temperature \( (T_{g,amorphous} < T_g < T_{g,crystalline}) \), the crystalline segment will not be affected by the temperature whereas the amorphous segment will be melted and will absorb the deformation. In the case of amorphous based shape memory polymer, when the temperature of the SMP will go below the glass transition temperature, the amorphous segments will begin to rearrange themselves but due to the presence of crystalline segment they will not be able to go back to the original shape and consequently, the deformation will be locked in.
ii. Melting Transition Temperature ($T_m$) (in the case of Crystalline Soft Segment)

The melting transition temperature is the temperature which is above the melting temperature of the soft crystalline segment ($T_{m, \text{soft crystalline}}$) but below the melting temperature of the hard crystalline segment ($T_{m, \text{hard crystalline}}$). In the case of melting transition temperature ($T > T_{m, \text{soft crystalline}}$), the soft crystalline segments of the polymer will be melted and will absorb the deformation. After applying deformation, if we lower the temperature of the deformed material below the melting transition temperature then strain-induced crystallization will occur. The formation of crystallization is always incomplete and certain amount of the chains remains amorphous. The amount of crystallites formed prevents the chains to go back to the deformed state and as a result, temporary shape is fixed.

The shape memory effect not only depends on the specific material property of a single polymer but it results from the combination of the polymer structure and morphology together with the applied processing and programming technology [Hu, 2007]. It is known that the macroscopic properties of polymer can be controlled by specific variation of molecular structure. This can be used to tailor the specific properties of shape memory polymer by slight variation in molecular structure [Lendlien & Kelch, 2002].

1.2.2.2. Shape Fixing and Recovering Process

The shape fixing, deformation, and recovery process of shape memory polymer are shown schematically in Figures 2 & 3 and the processes are described below:

1. At first, the polymer pellets have been heated above the melting point or glass transition temperature of the hard segment, $T_{gh}$. At this temperature, the polymer is in
viscous state and the cross-linking occurs. The corresponding shape is known as first synthetic form.

2. The synthetic form, which is also known as permanent shape, can be memorized by cooling the SMP below the melting point or glass transition temperature of the hard segment due to the formation of crystallization.

3. The polymer is heated above the glass transition temperature of the soft segment ($T_{gS}$) but below the transition temperature of the hard segment ($T_{gh}$). At this stage, the polymer will be in rubbery state. As a result, this will be able to accommodate a large amount of deformation. With the application of force, the polymer attains a shape, which is also known as secondary shape.

4. The secondary shape has been fixed by cooling the deformed SMP, under the
Figure 3: Schematic representation of the molecular mechanism of the thermally induced shape memory polymer
application of load, below the melting point or glass transition temperature of the soft segment ($T_{gs}$).

5. Finally, the original shape has been recovered by heating the material above the melting point or glass transition temperature of the soft segment ($T_{gs}$)

6. The recovered original shape has been cooled below the transition temperature of the soft segment in order to get the glassy state, since the modulus of the polymer is high at the glassy state.

Another method for setting a temporary shape involves the material being deformed at a temperature lower than the melting point or glass transition temperature of the soft segment. When the material is being heated above the melting point or glass transition temperature of the soft segment, the stresses, and strains are being relieved; and the material returns to its original shape [Hu, 2007].

In order to use the shape memory functionality of shape memory polymer, we need to program it which is also known as thermo-mechanical programming and it has been discussed in the following section.

1.2.2.3. Thermo-mechanical Programming

The various processes for thermo-mechanical programming of SMP are shown in Figure 4. For programming, the shape memory polymer is heated above the transition temperature, which can be glass transition or melting transition. At this temperature the shape memory polymer is in rubbery state and it can easily be deformed. In other words, it can accommodate deformation. Now at this stage, a force is applied on shape memory polymer, which induces strain in the polymer (process-1). After deforming, it is cooled below the transition temperature,
at which the switching segment becomes inactive and the polymer is in frozen or glassy state (process-2). After that, the applied load has been removed. On the removal of load, the polymer recovers some of its deformation due to elasticity behavior. But most of the deformation has been locked in and the polymer remains in the deformed state because of the decrease in temperature from above the transition to below the transition temperature (process-3). The resulting deformation creates a residual stress/strain which remains in the polymer until the recovery. Now at this stage if we heat the polymer above its glass transition temperature and it will go back to its original shape (process-4) [Lendlien & Behl, 2007].

**Figure 4:** Thermo-mechanical cycle of a thermally induced shape memory polymer [Lendlien & Behl, 2007]
After describing the structure, shape memory phenomena, and thermo-mechanical programming of shape memory polymer now it is time to discuss about the features of shape memory polymer. Before discussing the features of shape memory polymer, it is necessary to give a brief explanation of polymer, since the SMP, a kind of smart material, belongs to the large family of polymer.

1.2.2.4 Polymer

Polymers are large molecules made of smaller units. The large molecule is called a macromolecule. The name polymer emanates from greek: *poly* means many, *mer* means part. Thus, a monomer is a fundamental building block of a polymer. A polymer may consist of two parts in which case the molecule is a dimer. A polymer that has a few molecules is called an oligomer. Polymers occur in nature. Natural rubber is a polymer that has been extensively used for many products such as tires through the process of vulcanization, rubber bands among others. Other naturally occurring polymers include the deoxyribonucleic acid (DNA) – the purveyor of genetic information. The process of converting a monomer into a polymer is termed polymerization. Mainly polymers are classified into three groups according to the nature of the polymer [Shultz, 1974].

1.2.2.4.1 Thermoplastic Polymer

In thermoplastic polymer, molecules are held together by weak intermolecular forces. As a result, they soften when exposed to heat and solidifies upon cooling below the transition temperature. Thermoplastic polymers also can be classified into two groups:

i. Amorphous polymer

ii. Crystalline polymer
A brief description of amorphous and crystalline polymers is given below:

i. **Amorphous Polymer**

In amorphous polymer, the polymer chains are arranged in a random manner that is they did not follow any certain configuration due to the absence of crystallite or external force. Each configuration of polymer chain has the same amount of inner energy and the most probable one is the one with the highest entropy according to the Boltzmann Equation

\[
S = k \ln (W) \tag{1}
\]

where, \( S \) = Entropy

\[
k = \text{Boltzmann constant (1.3806503} \times 10^{-23} \text{ m}^2 \text{kgs}^{-2} \text{K}^{-1})
\]

\( W \) = Probability

ii. **Crystalline Polymer**

In crystalline polymer, the polymer chains are arranged in an ordered fashion and there exist crystallites, which hinder the movement of polymer chain. As a result, the polymer chains follow a certain configuration.

1.2.2.4.2 **Thermosetting polymer**

In thermosetting polymer, there exists a high degree of cross-linking between polymer chains, which restricts the movement of the polymer chain. As a result, thermosetting polymers are rigid and it is not possible to reshape upon heating.

1.2.2.4.3 **Elastomer**

Elastomers are rubbery materials that can be stretched several times of their un-stretched length upon the application of stress; and it will go back to its original shape upon the removal of
applied stress. Elastomer also possesses cross-linking which prevents the permanent movement of the polymer chain; but the degree of cross-linking is much less in comparison to thermosetting polymer. As a result, the polymer chains have some freedom to move.

A few important properties of polymer are discussed below:

1.2.2.5 Important Properties of Polymer

1.2.2.5.1 Visco-elastic Properties

The classical theory of elasticity deals with properties of perfectly elastic materials. This type of materials obeys Hooke’s law according to which stress is always proportional to strain but independent of the rate of strain.

In 1-D Hooke’s law can be written as:

\[ \sigma = E \varepsilon \]  \hspace{1cm} \text{Eq. (2)}

where, \( \sigma \) = stress (Pa)
\( \varepsilon \) = strain (mm/mm)
\( E \) = Young’s Modulus (Modulus of Elasticity) (Pa, N-m/s²)

On the other hand, according to the theory of hydrodynamics, which deals with the properties of perfectly viscous liquids, stress is always proportional to the rate of strain but independent of the strain. This is also known as Newton’s law, which can be written as:

\[ \sigma = \eta \frac{d\varepsilon}{dt} \]  \hspace{1cm} \text{Eq. (3)}

where, \( \sigma \) = stress (Pa)
Polymers are neither perfectly elastic nor perfectly viscous material. They show deviations from idealistic behavior. Their behavior can be attributed in between these two extremes. There exists two important types of deviations such as:

- The strain (in a solid) or the rate of strain (in a liquid) is not directly proportional to stress. In fact, there exists no clear relationship.
- The stress may depend on both the strain and the rate of strain as well as higher time derivative of strain.

Because of these deviations, polymer posses both solid as well as liquid like characteristics and are termed as visco-elastic material. Typically, in visco-elastic material, the relationship between stress and strain depends on time. The three most important visco-elastic properties of polymer are described below:

i. **Storage Modulus \( (E') \)**

Defined as the stress (which in phase with the strain in a sinusoidal shear deformation) divided by strain. It is a measure of the energy stored or energy recovered per cycle.

At long span of time \( E' \) approaches zero because the energy stored within the body becomes negligible compared to that lost by dissipation. In molecular level, \( E' \) depends on specific arrangement that takes place within the period of oscillatory deformation.

In mathematical form,

\[
E' = E^* \cos \delta
\]
where, \( E^* = \) complex modulus
\[ E' = \] storage modulus
\[ \delta = \text{angle of phase- shift between stress and strain (rad)} \]

ii. **Loss Modulus (E")**

Defined as the stress (which is out of phase with the strain in a sinusoidal shear deformation) divided by the strain. It is the measure of the loss of energy dissipated by heat per cycle and it is usually denoted by \( E'' \).

At high frequency, the loss modulus approaches zero which, on a molecular basis corresponds to the absence of any molecular or atomic rearrangement capable of dissipating energy within the period of time.

In mathematical form,
\[ E'' = E^* \sin \delta \]

where, \( E^* = \) complex modulus
\[ E'' = \] loss modulus
\[ \delta = \text{angle of phase- shift between stress and strain (rad)} \]

iii. **Tan delta (Tan \( \delta \))**

This is defined as the ratio of loss modulus to storage modulus. In other word, it represents the damping capacity of the material.

\[ Tan \ \delta = \frac{E''}{E'} = \frac{Loss \ Modulus}{Storage \ Modulus} \]

Other important parameters of visco-elastic material are described below:
**Complex Modulus (E*)**

This is defined as the ratio of stress vs. strain at constant deformation.

At short time, $E^*$ approaches to a limiting value, which represents the rigidity of the molecule in the absence of molecular rearrangement of the backbone of molecules. At long time $E^*$ falls rapidly and eventually goes to a zero value. It is because of the random rearrangement of the molecular chains from the constraints, which has been initially placed on the chains by the application of external stress.

The stress-strain relation for visco-elastic materials is:

$$\sigma = \varepsilon E^* = \varepsilon (E' + iE'') = \varepsilon_0 \sin(\omega t + \delta) \sin (\omega t + \delta) = \sigma_0 \sin (\omega t + \delta)$$  \hspace{1cm} Eq. (4)

where,  

$\sigma$ = stress (Pa)  

$\varepsilon$ = strain (mm/mm)  

$E^*$ = complex modulus (Pa, N·m/s²)  

$E'$ = storage modulus (Pa, N·m/s²)  

$E''$ = loss modulus (Pa, N·m/s²)  

$\delta$ = angle of phase-shift between stress and strain (rad)  

$\omega$ = angular frequency (rad/s)  

$t$ = time (s)  

$i$ = complex number
In dynamic mechanical analysis, a small sinusoidal deformation is applied to the polymer and because of small deformation, the material remains always within the elastic region. For a perfectly elastic material, the stress and strain are in phase as they are directly proportional as shown in Figure 5 below.

![Figure 5: Force-displacement relationship of perfectly elastic material under dynamic force](image)

On the other hand, for perfectly viscous materials stress and strain are $90^\circ$ out of phase as stress is proportional to the rate of strain as shown in Figure 6.

![Figure 6: Force-displacement relationship for viscous material under dynamic force](image)
Most polymeric materials show both elastic and viscous behavior that is they act as a glassy material and at the same time they flow to a some extent. Therefore, the phase difference between stress and strain is neither $0^\circ$ nor $90^\circ$. Rather it falls between $0^\circ$ and $90^\circ$. The stress and strain behavior of visco-elastic material under dynamic mechanical analysis is shown above in Figure 7.

1.2.2.5.2 Transition Temperature

As the temperature of polymer increases most of the polymer chains begin to relax and move. As a result, free volume of polymer increases significantly which is accompanied by drastic change in property. The glass transition temperature is the temperature at which the polymer undergoes a drastic change in the property such as mechanical, electrical, thermal, or other electrical property. The glass transition temperature is dependent on the degree of
crystallinity of the polymer and it is one of the major transitions of polymer. The glass transition temperature can be determined by DSC (Differential Scanning Calorimetry) or by DMA (Dynamic Mechanical Analyzer).

Though SMP belongs to the family of polymer, not all the polymers shows shape memory property. In order to have shape memory functionality, the polymers must possess some special characteristics. The groups of polymers are capable to show shape memory properties are discussed below:

**1.2.2.6 Class of Polymers Showing Shape Memory Property**

So far, many polymers have been invented which possess the shape memory capability. In general, shape memory polymer can be divided into four categories [Liu et al., 2007] such as:

**1.2.2.6.1 Chemically Cross- linked Glassy Thermosets**

This is chemically cross-linked glassy polymer which shows sharp transition temperature and rubber elasticity above the transition temperature. The cross-linking can be achieved by polymerization, polycondensation or polyaddition. On the application of external force above the Tg, the polymer undergoes deformation which leads to secondary shape. The secondary shape can be fixed by cooling below the Tg due to the decrease in mobility of molecules. The original shape can be recovered by the reheating the polymer above the transition temperature. This type of polymer shows complete shape-fixing through vitrification and fast recovery due to the sharp transition temperature. Examples include polystyrene copolymer [Tong, 2002], poly (alkyl methacrylate) co-polymers, chemically cross-linked amorphous polyurethanes, biodegradable copolyester urethane networks, poly (methyl methacrylate) -co- ( N-vinyl-2-pyrrolidone) – PEG semi-IPN [Liu et al., 2006] etc.
1.2.2.6.2 Chemically Cross-linked Semi-crystalline Polymer

In this class of polymer, the melting transition of semi-crystalline networks acts as the transition temperature. The shape memory effect is similar to that of class-I apart from the fact that the secondary shape is fixed by the crystallization instead of vitrification. Examples of this class of polymer include chemically cross-linked trans-polyisoprene (TIP) [Irie et al., 1998], oligomeric poly (ε-caprolactone) dimethacrylate with n-butyl acrylate [Lendlien et al., 2001] etc.

1.2.2.6.3 Physically Cross-linked Glassy Copolymer

Here, shape memory effect is the result of the formation of phase segregated morphology. Between the two phases which has the lowest transition temperature acts as the molecular switch. On the other hand, the phase, which has the highest transition temperature, is responsible for retaining the permanent shape and providing mechanical strength due to the absence of chemical cross-linking this type of polymers can be processed very easily. Examples include melt-miscible blend of poly (vinyl acetate) and poly (lactic acid) [Jeong et al., 2001], Polyurethane with poly (ε-caprolactone), Polystyrene and poly (1,4 butadiene) [Kithara & Nigata, 1991] etc.

1.2.2.6.4 Physically Cross-linked Semi-crystalline Block Copolymers

In this class of block copolymer the soft domains crystallize below the transition temperature and their melting temperature, $T_m$ acts as transition temperature instead of glass transition temperature, $T_g$. Examples include Styrene-trans-butadiene-styrene (STBS) triblock copolymer [Ikematsu et al., 1990], PEO based multiblock polyurethane [Korley et al., 2006] etc.

At this stage, we give a brief introduction of polymer, some of its important properties and the classes of polymer, which are capable to show shape memory property. Finally, we are
now at a stage to discuss about the parameters for characterizing the shape memory properties of a polymer.

1.2.2.7 Parameters for Characterization

In order to characterize the shape memory properties of polymer a set of parameters has been introduced. These parameters are able to reflect the nature of polymers and at the same differentiate them from other properties of materials [Tobushi et al., 1996]. A brief introduction of these parameters is given below:

1.2.2.7.1 Strain Recovery Rate

It is a measure of the ability of a material to memorize its permanent shape [Tobushi et al., 1996].

\[
R_r(N) = \frac{\epsilon_m - \epsilon_p(N)}{\epsilon_m - \epsilon_p(N-1)} \quad \text{Eq. (5)}
\]

where, \(\epsilon_m\) = the maximum strain (mm/mm)

\(\epsilon_p(N)\) = residual strain after heating at \(T_h\) in the Nth cycle (mm/mm)

\(\epsilon_p(N)\) = residual strain after heating at \(T_h\) in the (N-1)th cycle (mm/mm)

\(T_h = [T_g + 20 \, ^\circC]\) (°C)

1.2.2.7.2 Shape Fixity Rate

It is a measure of how exactly the sample can fix the stretched shape after a deformation to a strain value of \(\epsilon_m\). The resulting- deformed shape is always different than the stretched shape [Tobushi et al., 1996].
Shape Fixity, \( R_f(N) = \frac{Fixed \ deformation}{Total \ deformation} \)

\[
R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \quad \text{Eq. (6)}
\]

where, \( \varepsilon_u(N) \) = the strain at the termination point of unloading (mm/mm)

\( \varepsilon_m \) = the maximum strain (mm/mm)

### 1.2.2.7.3 Recovery Rate

This is defined as the rate at which the SMP returns to its original shape. In other word, it tells us how fast the deformed shape will go to its original shape upon heating the SMP above the transition temperature.

\[
V_r = \frac{dR_r}{dT} \times \frac{dT}{dt} \quad \text{Eq. (7)}
\]

where, \( V_r = \) shape recovery speed (m/s)

\[
\frac{dR_r}{dT} = \text{the ratio of shape recovery to temp}
\]

\[
\frac{dT}{dt} = \text{the increasing rate of temperature with time}
\]

### 1.2.2.7.4 Recovery Stress

At temperature above the transition temperature the SMP are in rubbery state. As a result, it will be able to accommodate a large amount of deformation. When the SMP is heated and deformed above the transition temperature the elastic stress is generated within the SMP. Upon cooling the SMP below the transition temperature this elastic stress is stored. When we heat the deformed SMP above the transition temperature again the SMP will recover its original shape.
During the process of recovery of original shape the stored elastic energy will be released which is known as recovery stress [Tobushi et al., 2001].

1.3 Research Objectives

Shape memory polymers exhibit a unique combination of low density, higher recoverable strain, and shape memory behavior that gives them a wide range of potential applications. The majority of proposed applications are in the biomedical field where the biodegradability of the shape memory polymer offsets relatively lower recovery force compared to shape memory alloys. The reason motivating this application is highly compact, storable structures with shape memory capability to be used as transplant or as an auxiliary medium. Other applications include space deployable structure, data storage device, heat shrinkable tubing etc. Before the potential application of shape memory polymers can be reached work must be performed to characterize the effect of environmental factors on the properties of shape memory polymer. Once this understanding has been reached, models need to be improved so industry can efficiently select shape memory polymer into new and existing application according to the needs of applications.

Although prior works have considered the effect of limited environmental factors on shape memory polymers, but they have not considered a comprehensive set of environmental factors. In addition, earlier work focuses on polyurethane based shape memory polymers, which are either amorphous or multiblock copolymer polyurethanes. Furthermore, they did not investigate the changes in molecular structure due to the various environmental factors in a more elaborate way.

The main purpose of this thesis is to provide a more thorough understanding of the effect of environmental factors on shape memory polymer such as the effect of frequency, thermo-
mechanical cycle, water absorption, moisture, heat treatment, and dynamic loading. Moreover, the combination of dynamic mechanical loading, Fourier transform infrared spectroscopy and macroscopic thermo-mechanical tests will be used to help understand the linkage between the molecular structure and the bulk properties of shape memory polymer.

1.4 Outline of the Thesis

In this thesis, we seek to study the degradation behavior of styrene based shape memory polymer (Veriflex- SMP from Corner Stone Research Group) due to prolonged immersion in water and diesel fuel separately.

Chapter 2 starts with the history of shape memory polymer. After that, a brief overview about the application of SMP in various fields has been given. Then the efforts of researchers to characterize the shape memory polymer from various points of view has been discussed and critically reviewed. Finally, it ends with giving the motivation and conclusion behind this research deriving from the literature review.

Chapter 3 describes the experimental procedure. At first the polymer and solvent used in this research have been introduced. Then a brief introduction on various equipments and clamps used in this research has been given. Finally, it ends by giving a detail expression about the procedure of various experiments, which have been carried out in this research.

Chapter 4 describes the results of various experiments. At first, the shape memory property of the Veriflex- SMP has been determined by defining characteristics of shape memory polymer. Then the recovery force generated by Veriflex- SMP has been determined. After that, the degradation of Veriflex- SMP due to immersion in water and diesel fuel has been discussed. Finally, the FTIR results on untreated and treated Veriflex- SMP have been discussed.
Chapter 5 describes the conclusion from the results obtained from experimental studies in this thesis and finally, a few recommendations for future research have been proposed.

1.5 References


2 LITERATURE REVIEW

2.1 History

From literature review it is known that the shape memory effect has been first discovered by Chang and Read in 1932 [Chang & Read, 1951]. The discovery of shape memory effect is one of the revolutionary steps in the area of smart material. Shape memory materials are a type of smart material that has the ability to maintain the deformed shape and again to recover the original shape upon the application of external stimulus such as temperature, light etc. Among them, thermally responsive shape memory materials are the most notable one, in which the recovery takes place upon heating it above a certain temperature, which is called the transition temperature. The most commonly used shape memory material is NiTi alloy which is formally known as shape memory alloy (SMA) [Buhler et al., 1963]. NiTi alloy has some notable properties such as small size, high strength [Wei et al., 1998] etc. However, disadvantages for example, low recoverable ratio, high manufacturing cost, and toxicity limits their uses. Therefore, scientists and researchers begin to look for new materials, which have the shape memory effect but do not possess these disadvantages. As a result of this unending quest of researchers shape memory ceramics [Swiain, 1986] and shape memory polymers [Yu & Ikeda, 2005] have been explored.

According to Sakurai et al. [Sakurai & Takahashi, 1989] the first SMP, developed by the French CDF Chimie company and commercialized by Nippon Zeon Co. in Japan, was polynorbornene based SMP with the glass transition temperature, Tg ranging from 35°C to 40°C. This range of transition temperature, T_g makes it suitable for developing apparel textiles. However, the molecular weight of this polymer is very high which makes it difficult for processing. Later Kurray company in Japan developed a transpolyisoprene based SMP with a T_g
of 67°C in 1987. Asahi company also introduced a styrene-butadiene based SMP with the \( T_g \) ranging from 60°C to 90°C [Shizuo & Nobuo, 1991]. The high transition temperature, \( T_g \) of this two types of SMP serves them as a good candidate for high temperature application but limit their usefulness in apparel textile. Finally Mitsubishi Heavy Industry (MHI) developed a polyurethane based thermoplastic polymers (SMPU) with transition temperature, \( T_g \) ranging from -30°C to +65°C. Apart from that, the processibility of SMPU is also very easy [Hayashi & Shirai, 1988].

Since the discovery, SMP have drawn increasing attention because of its high recoverable ratio, low cost, low weight, and wide range of mechanical properties as compared to SMAs or ceramics [Liu et al., 2007]. Generally SMP is a thermally sensitive material but it also can be stimulated by electrically [Vaia, 2005], magnetically [Razzaq et al., 2007], electromagnetically [Maitland et al., 2002] by incorporating associated functional group in the polymer. Recently light- induced [Lendlien et al., 2005] and UV- induced [Finklemann et al., 2001] SMP have been discovered.

### 2.2 Application of Shape Memory Polymer

Now- a- days, SMP is used in almost every area of our daily life including kitchen utensils, switches, sensors, intelligent packing, heat-shrinkable tubing [Kleinhans et al., 1986], space and medical applications, smart structural repair, reconfigurable-tooling [Dietsch & Tong, 2007], micro-electromechanical systems, actuators, self-healing, health monitoring, biomedical devices [Chaterji et al., 2007], bio sensors [Ratna & Karger-Kocsis, 2008], and self-repairing auto bodies [Dietsch & Tong, 2007]. Some important applications are discussed briefly:
2.2.1 Biomedical Applications

(i) In the health-care for dialysis patients in the US costs around $1 billion due to the complications of vascular access resulting from graft failure. Recently, it has been discovered that hemodynamic stress from dialysis needle has play a prominent role in graft failure. In the article, it was proposed a method to reduce the hemodynamic stress in an AV graft with the help of deployable SMP dialysis needle adapter, which will tailor the fluid dynamics of the venous needle flow. At first, this adapter is deployed in the graft through the needle in compact form. Then it is allowed to expand using thermal energy and the distal end of the adapter has a large cross sectional area than that of the needle as shown in Figure 8.

![Figure 8](image)

**Figure 8:** Time average velocity of streamline from a) without a needle and b) with a needle of SMP [Ortega et al., 2007]

Because of the SMP adapter, the jet from the needle is oriented in the downstream and does not flow severely. Furthermore, the larger cross sectional area of the needle reduces the speed of the jet. As a result, the hemodynamic stress on the graft has been reduced significantly. At the end of the dialysis session, the adapter is retracted through the needle. [Ortega et al., 2007]
About 600,000 people in the US have suffered from ischemic stroke each year. The formation of blood clot, which is known as thrombotic vascular occlusion, in the arterial network which prevents the supply of blood to the brain are the main reason for ischemic stroke. The brain suffers from oxygen due to the interruption of blood flow. Previously recombinant tissue plasminogen activator (t-PA) has been used to restore the blood circulation, which chemically dissolves the blood clot. However, this treatment must be initiated within three hours of the onset of symptoms. Another disadvantage of this treatment is the risk of intracranial hemorrhage. In the article [Kleinhans et al., 1986] it was mentioned that the developed intravascular device made of SMP which will physically capture the thrombus, remove and restore the blood flow within a few minutes rather than hours as shown in Figure 9.

Figure 9: Removal of thrombotic vascular occlusion [Small et al., 2005]

In addition the longer treatment window will reduce the risk of intracranial hemorrhage. In their model the SMP has been deployed in straight rod form to the vascular occlusion under fluoroscopic guidance through a catheter distal. Then the SMP device has been actuated by laser
heating to go back into corkscrew shape, which is primary shape of the SMP device. It then captures the thrombus with the help of its primary shape. Finally, the SMP device along with captured thrombus has been retracted through the catheter, and the blood flow has been restored. [Small et al., 2005]

### 2.2.2 Space Applications

One of the major drawbacks of space structure is its large size and huge cost of manufacturing. Most of the researches on space structure have been focused into developing higher capability space structure at low cost and of small size. In addition, it is expected that within the next few years the size of the spacecraft will become into the size of a single microchip. However, some of the subsystem requires larger size to do their function such as space antenna will have to be larger size. Otherwise, the rate of data communication will be slow. Further mobile communication satellite should have to be large enough to provide the access of multiple users. This dilemma creates the idea that spacecraft should be built small in size. While after deployment, the space structure should convert into the expandable form. Recently National Aeronautics and Space Administration (NASA) and the Department of Defense (DoD) develop a simple, reliable, and low cost expandable structure which is known as Cold Hibernated Elastic Memory (CHEM). SMPs are regarded as one of the major components in the manufacturing of CHEM structures, because of its capability to memorize the permanent shape upon the application of external stimulus such as heat. Another potential advantage of SMP is the wide range of glass transition temperature. Depending on the end application, the transition temperature of CHEM structures can have different values. As an example, the Tg of CHEM structure for warmer terrestrial application can be 50°C or higher whereas for the Mars Pathfinder mission it is nearer to 0°C. [Sokolowski et al., 1999]
2.2.3 Structural Applications

The exceptional ability of Geckos to climb up rapidly in smooth vertical surfaces has attracts scientists and researchers a lot from the very beginning. Recently scientists have been able to discover the mechanism behind this ability. The toes of gecko are comprised millions of submicrometre keratin hairs which all together produce a force of the magnitude of 10 N cm\(^2\). Inspiring from this phenomena scientists have developed an adhesive, which is known as Gecko tape made from dense arrays of flexible plastic pillars through micro-fabrication. [Geim et al., 2003]. One of the major drawbacks of Gecko adhesive is its reliability on external forces for detachment. In the article [Small et al., 2005] it was mentioned to propose a self-peeling reversible dry adhesive (SPRA) with self-reversal capability.

The adhesive made from a shape memory polymer layer (T\(_g\) = 39.9°C) and a smooth (nanostructured) dry adhesive layer (T\(_g\) = 3°C). The newly formed adhesive has low cost but strong adhesion coefficient and high durability.

The Figure 10 below represents the double layer construction of SPRA which has a slight curvature due to the chemical shrinkage during the curing and the difference in thermal expansion coefficient of the two layers. Due to the curvature, the SPRA has a poor contact. Therefore, it is heated above the transition temperature of the SMP and a preload is applied to comply with the surface profile of the substrate. Then it is cooled below the transition temperature and the preload has been removed and the result is a good contact between the adhesive and the substrate. The sample has been heated above the T\(_g\) of SMP to debond instead of applying pull-off force. Due to heating and shape memory property of SMP the SPRA transforms to curvature again and the contact area between SPRA and the Substrate has become
less. The sample has separated using a small amount of force, which is less than 0.1 N/cm. [Xie & Xiao, 2008]

#### Figure 10: Self-peeling reversible bonding system [Xie & Xiao, 2008]

2.2.4 Textile Applications

The application of SMP in clothing relies on its functional properties such as smart clothing, which will not need ironing, and it will interact with the change in environment.

Mitsubishi Heavy Industries developed one kind of such smart cloth, which is named ‘Diaplex’ by placing SMP laminate between two layers of fabric and is shown in Figure 11. It uses the micro-Brownian motion of polymer chains to act as an intelligent material. When the body temperature is below a certain temperature then the molecular structure is rigid which lowers the permeability. As a result, heat cannot escape and the body temperature is kept at a comfort level.
On the other hand, when the body temperature raises above a certain level the Micro-Brownian motion increases. The increase of Micro-Brownian motion increases permeability and allows air and water molecule to pass through it to the outside environment. In this way, it removes excess heat of the body. [http://www.diaplex.com]

### 2.3 Progress of Research in Shape Memory Polymer

To fully utilize the shape memory functionality of shape memory polymer and explore new area for application of shape memory polymer demands thorough characterization. In addition, we have to understand the fundamental understanding of the relationship between polymer structure and corresponding shape memory characteristics. This understanding will also help us in acquiring optimized shape recovery properties.

So far, significant amount of research have been done in the area of characterization of SMP. Ken Gall et al. [Gall et al., 2004], have developed acrylate based SMP and found that with...
the increase of cross-linking agent the stiffness of the polymer increases. The recoverable strain of the SMP can be up to 80%. At first, the SMP has been deformed above the transition temperature and then it is cooled to fix the deformation. While cooling under constant strain, the stress decreases due to thermal contraction governed by the thermal expansion coefficient. The deformation of material near \( T_g \) changes the conformation of the polymer chain which results in the storage of internal energy. During cooling at constant strain level, the free-volume available to polymer chains decreases which forces the polymer chains to form secondary bonding. The drop in the external stress represents a metastable phase with reduced entropy and high internal energy. At this stage, the cross-linking points serves as an anchor point to prevent the chains from slipping past one another. Upon heating, the internal energy is released and the material goes back to the un-deformed state with the increase of entropy. At first, a gradual recovery occurs due to thermal expansion. However, upon reaching the transition temperature a large-scale strain recovery occurs. Gall et al. observed that recovery under constraint occurs and completes at a lower temperature relative to free strain recovery [Gall et al., 2004]. This may be due to the increase of stress associated with thermal expansion. Upon further heating, the stress reaches at equilibrium position governed by the high temperature stress-strain relationship.

Yakacki et al. [Yakacki et al., 2008] have investigated the effect of network structure and deformation parameter on the strain limits of shape memory polymer. They found that there is no effect of heating rate on the glass transition temperature where as the change in frequency alters the glass transition temperature. The SMP will accommodate maximum amount of deformation if it is deformed near the onset of glass transition temperature. It also depends on the cross-linking density of the network structure. Gall et al. [Gall et al., 2005] have found that the deformation temperature, \( T_d \) and the recovery temperature, \( T_r \) have a strong influence on the
recovery behavior of shape memory polymer. Takahashi et al. [Takahashi et al., 1996] have studied the thermal transition and shape recovery behavior by tailoring the macromolecular properties and relative fractions of hard and soft segments of SMP.

Gunes et al., 2008 analyzed the thermal expansion behavior of SMP. The change of length with temperature exhibits three different regions such as below and above the melting point of soft segment, and the transitions between them. In the region above and below the melting point of soft segment the behavior of CTE (coefficient of thermal expansion) is linear which represents the state of thermodynamic equilibrium. They suggested that for SMPs capable of recovering high amount of strain (>10%), the effect of thermal expansion can be neglected during the constitutive modeling. On the other hand, if it is considered then care should be given into the linear and nonlinear behavior of CTE.

Tobushi et al., 2004 found that long-term behaviors of SMP are not perfect. Due to thermal motion of the molecular chain of the SMP, a rearrangement of the molecular chains occur if it is held for a long time at a high temperature and under large strain. The effect of holding temperature, holding time and holding strain have a significant effect on the strain holding condition. Tobushi et al., 2006 have found that SMP will show irrecoverable strain if the strain is held above the transition temperature. The amount of irrecoverable strain will increase with the increase of holding time, $T_h$ and the amount of initial strain. To avoid irrecoverable strain and secondary shape forming, they suggest holding the strain below the transition temperature. On the contrary, to form secondary shape, the strain should be held above the transition temperature.

Meng Q. et al., 2009 have studied the effect of heat treatment on Shape Memory Fibers.
In polymer the chain segments are flexible and able to rotate to form an orderly conformation of structure. The application of heat treatment decreases chain entanglement and improves the ability of the polymer to crystallize. Also, the internal stress stored in the hard segment phase during the deformation stage and the disorientation of soft segment phase decreases. With the increase of heat treatment temperature, most of the disorientation of soft segment has been vanished and the soft segment phase becomes a stable one. Also, the separation between the soft phase and hard phase increases with the application of heat treatment.

Lorenzo et al., 2009 have studied the effect of physical aging on SMP. The SMP usually consists of two phases: fixed phase and soft phase. Fixed phase is responsible to recover the primary shape whereas the soft phase is responsible to fix the deformed shape. When we heat the SMP to a temperature above the glass transition temperature, it becomes a rubbery-like material, and it will deform in the direction of applied force with a loss of entropy. This deformed shape will be fixed when we cool the material below the glass transition temperature under the constraint. In this deformed state, the polymer is in a metastable state and with the passage of time, it relax towards equilibrium state. As a result, glass transition temperature increases because a higher amount of energy is required to melt the soft phase segment. During the relaxation, specific volume and enthalpy decreases while mechanical properties such as modulus of elasticity and hardness increases.

Hu et al., 2005 have studied the effect of thermo-mechanical cyclic condition on SMP. If the deformation temperature is much lower in comparison to the glass transition temperature then both the fixed phase and the soft phase are rigid and the SMP will not go back to its original shape. Because the phase which is responsible for memorizing the shape, fixed phase, has been deformed. If the deformation temperature is above the glass transition temperature of the soft
phase but below the fixed phase, then the soft phase has enough mobility and the whole
deformation will be taken by soft phase. It has been observed that SMP will show a good
recovery ratio if it is deformed in a temperature range where the soft phase has sufficient
mobility and the fixed phase are relatively stable.

The influence of hard segment content has been studied by Mondal & Hu, 2007. The
storage modulus increases with the increase of hard segment. If the amount of hard segment is
more, then the reinforcing-effect of hard segment in soft segment matrix will be more. As a
result, it will increase the cohesion between the hard segment and the soft segment. Also hard
segment content hinders the movement of soft segment, which causes the polymer to become
more brittle. On the other hand, tan delta term decreases with the increase of soft segment
content, because of the increasing rate of the flexibility of the soft segment chain molecule.

The behavior of SMP subjected to tension and shear stress have been studied by
Pieczyska et al., 2008. At first there was a linear relationship exists between stress and strain.
After that, some localized deformation occurs at the specimen, which was observed by infrared
camera. With the increase of loading, the localized deformation increases that can be observed
by naked eye due to the existence of some bands and white color which is known as crazing.
Finally, necking appears at the specimen. At the place of deformation, temperature increases but
the average temperature of the sample remains same. At this level if we increase the temperature
above the transition temperature, $T_g$ the localization will disappear which verify the shape
memory property. In case of tensile test, the localization observed at comparatively lower strain
rates but in the case of shear deformation, the localization appears at higher strain rates.

Haibao et al., 2008 have examined the effect of solution on the actuation of SMP. Due to
the immersion of SMP in solution the storage modulus and transition temperature have been decreased. The interaction between the micromolecule of absorbed solution with macromolecule of polymer weakens the elastic modulus which reduces the transition temperature. They also observed the loss of mechanical property of polymer due to the formation of hydrogen bonding which increases the flexibility of polymeric molecular chains.

Tey et al., 2001 have been found that shape memory polymer will regain its shape in 4-days if it is stored in ambient room condition without any constraint placed on it; which is in contrary of the result of Hayashi et al., 1988. The shape memory mechanism of shape memory alloy is the transformation in terms of microstructure change through phase transformation or martensite orientation. Therefore, we can expect that a higher amount of force will generate when we heat the specimen to a higher temperature above the glass transition temperature. However, in the case of shape memory polymer the driving force for shape memory effect is the micro-Brownian movement above the glass transition temperature. The phases of SMP become more softened with the increase of temperature above the glass transition temperature. As a result, we will not get higher force at higher temperature above the glass transition temperature.

Yang et al., 2006 have found that the glass transition temperature ($T_g$) of shape memory polymer decreases with the increase of immersion time because absorbed water weakens the hydrogen bonding between different functional groups. As a result, soft segment molecules are able to move freely. The rate of decreasing is higher at initial stage. After a certain interval of time the glass transition temperature becomes stable that is the absorption of water reach a saturation level. Water absorbed in SMP can be divided into two parts: free water and bound water. Free water does not have a significant effect on the property of shape memory polymer. While bound water decreases the glass transition temperature almost linearly and it affects the
tensile behavior of SMP. When the immersion time is shorter, then it behaves as a solid material but with the increase of immersion time, it becomes rubbery-like material.

2.4 Conclusion from the Literature Review

In conclusion, previous researches mainly focused on thermal transition, \( T_g \), thermomechanical, and shape memory properties of SMP. Nevertheless, we know that SMP is a viscoelastic material and the properties of visco-elastic material depend strongly on time. In order to explore possible applications of SMP, it is necessary to determine the material resistance against various environmental factors. The properties of SMP may change because of degradation, and ultimately to the point where the material will be no longer be capable of satisfying its function. The extent of degradation is dependent on many factors including polymer nature and environmental conditions. Huang et al., 2005 have examined the effect of moisture on the glass transition temperature and shape memory property of SMP. Yang et al., 2006 have found that the glass transition temperature of the polymer decreases and ultimately the SMP losses its shape fixing capability if it is left in air at room temperature for several days. They also found that the absorption of moisture mainly causes the change. This kind of results gives us the motivation to investigate further the effect of water and solvent on the property of SMP. After conducting degradation tests the materials physical and shape memory properties have been analyzed at regular intervals. The purpose of this work is to develop an understanding of the degradation processes that may have a significant role in the stress relaxation process.

2.5 References


http://www.diaplex.com


3 EXPERIMENTAL METHODS

A brief description of material, outline of experiments, equipment, and experimental methods are given in this section. At first, the shape memory property of styrene based Veriflex-SMP has been investigated. After that, a set of experiments to investigate the degradation behavior of SMP due to water and diesel fuel has been carried out.

3.1 Materials

The shape memory polymer that has been used in this study can be described by following a particular direction. The transition temperature, $T_g$ of SMP can be tailored according to the need by varying manufacturing conditions and quantity of each constituent. In general, the SMP can be manufactured by mixing one reagent containing two active amino hydrogen or two active phenolic hydrogen with at least one multifunctional cross-linking reagent which contains at least three or more active amino or phenolic-hydrogen. The mixture is further mixed with at least one difunctional epoxide. In this case the shape memory polymer (SMP) is the product of reaction between (a) styrene, (b) a vinyl compound other than styrene, (c) a cross linking agent and (d) an initiator. By varying the composition of each component, the $T_g$ of SMP can be tailored to the required application. The system with two different monomers is called a copolymer.

The proposed components and curing cycle are:

a) Styrene – 90% (1st monomer, styrene)

b) Vinyl neodecanoate – 7% (2nd monomer, vinyl compound)

c) Divinyl benzene – 1% (cross-linking agent)

d) Benzoyl peroxide – 2% (initiator)
The above-mentioned constituents are mixed in the specified order and refrigerated before use. The refrigerated mixture is then polymerized preferably in the temperature range of 65°C to

where, $R = C_9H_{19}$

**Figure 12:** Cross-linking process during the polymerization of the Polystyrene SMP [Ref: Manu John, 2009].
Figure 13: Free Radical Initiation and Polymerization Process [Ref: Manu John, 2010]
use. The refrigerated mixture is then polymerized preferably in the temperature range of 65°C to 75°C and at a pressure of 14.7 psi for about 4 hours to 30 hrs. It is further cured at 75°C for 24 hours by injecting it into a mold. After the end of curing cycle the SMP sheet is demolded and the samples of the desired dimension have been cut from the sheet.

3.1.1 Polymerization Process

There are three monomers namely styrene, vinyl neodecanoate and Divinyl benzene in Part- A of the veriflex shape memory polymer system. Divinyl benzene acts as a cross-linking agent, which helps in cross-linking the other two monomers as shown in Figure 12.

When Benzoyl peroxide (Part- B of veriflex), the initiator, is mixed with part- A, a free radical initiation process starts which is shown in Figure 13. The process consists of several stages, which is depicted in the Figure 13 below. In the first stage, free radical generates from Benzoyl peroxide. In the next stage, the free radical thus generated reacts with one of the monomers in part- A and is known as Chain Initiation process. In the last stage, either of the remaining two polymers reacts with the secondary radical to form the final shape memory polymer, which is called Chain Propagation.

3.1.2 Properties of Material

Some important properties of styrene based Veriflex- SMP supplied by manufacturer (Cornerstone Research Group) (Data taken from [http://www.crg-industries.com/datasheets/Veriflex-resin.pdf](http://www.crg-industries.com/datasheets/Veriflex-resin.pdf) is given below:

- Tensile strength (ultimate) 23 MPa
- Tensile modulus 1.24 GPa
- Flexural strength 37.1 MPa
• Flexural modulus 1.24 GPa
• Compressive strength 32.4 MPa
• Compressive modulus 1.45 GPa
• Thermal conductivity 0.17 W/(m·°K)
• Tensile elongation to break 3.9%
• Glass transition temperature 143°F (62°C)
• Thermal conductivity 0.17 W/(m·°K)
• Material density 0.92 g/cm³

3.2 Outline of Experiments

In real-life applications, the shape memory polymer may come in contact with various types of environmental agents and could also be used in different types of environmental conditions. Some environment may not be quite dangerous to the SMP. However, some may deteriorate the property of SMP. It may attack the polymer and causes degradation to its property. As we know, the degradation process of polymer is of two types:

i. Physical

ii. Chemical

To investigate the effect of degradation we used only two different types of solvent: water and diesel fuel.

i. Water

In this research, distilled water at room temperature has been used. Moisture is an integral part of environment. It varies from 10% to 100% depending on the weather condition. If our polymer indicates that it is sensitive to moisture, water absorption will occur and the properties
of Veriflex- SMP will be deteriorated. Although, many research have been done on the investigation of water on the properties of SMP, all researches have been done on Polyurethane based SMP. According to the knowledge of the author, no research has been carried out on Styrene based SMP. It may be possible that the effect of water on styrene based SMP will be the same as that on the polyurethane based SMP. In that case, the result of previous research may act as a verification of our experimental procedure, the result will verify the effect of other solvent.

ii. Diesel fuel

In this research, automotive diesel fuel has been used as another solvent, which is a strong solvent and can deteriorate the property of SMP drastically. During the lifetime, the SMP may be exposed to diesel. In that case, if it fails then it may cause catastrophic failure. So for designing new application of SMP, the effect of diesel fuel on its property must be considered. To aid in that respect we select diesel fuel as another solvent.

To investigate the effect of each type of degradation on SMP we performed the following set of experiments:

**Table 1: List of experiments performed**

<table>
<thead>
<tr>
<th>Experiments performed</th>
<th>Purpose of the experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermo-mechanical cycle</td>
<td>Change in shape memory properties</td>
</tr>
<tr>
<td>Dynamic mechanical thermal analysis</td>
<td>Change in dynamic mechanical properties</td>
</tr>
<tr>
<td>Stress relaxation test</td>
<td>Change in stress relaxation</td>
</tr>
<tr>
<td>Fourier transform infrared test</td>
<td>Change in molecular conformational structure</td>
</tr>
</tbody>
</table>
The experiments to investigate the effects of the amount of degradation due to water and diesel fuel separately on styrene based SMPs were treated by the methods shown in the following Table 2. Our main purpose is to investigate the effect of solvent for up to one month. All treatments have been done at room temperature. After the pre-treatment, the samples were stored in polythene zipper bag at room temperature until subsequent testing.

Table 2: SMP pre-treatment procedure

<table>
<thead>
<tr>
<th>Number of Treatments</th>
<th>Treatment Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>immersed in 50 ml. distilled water for 1 week</td>
</tr>
<tr>
<td>2</td>
<td>immersed in 50 ml. distilled water for 2 weeks</td>
</tr>
<tr>
<td>3</td>
<td>immersed in 50 ml. distilled water for 3 weeks</td>
</tr>
<tr>
<td>4</td>
<td>immersed in 50 ml. distilled water for 4 weeks</td>
</tr>
<tr>
<td>5</td>
<td>immersed in 50 ml. distilled water for 8 weeks</td>
</tr>
<tr>
<td>6</td>
<td>immersed in 50 ml. diesel fuel for 1 week</td>
</tr>
<tr>
<td>7</td>
<td>immersed in 50 ml. diesel fuel for 2 weeks</td>
</tr>
<tr>
<td>8</td>
<td>immersed in 50 ml. diesel fuel for 3 weeks</td>
</tr>
<tr>
<td>9</td>
<td>immersed in 50 ml. diesel fuel for 4 weeks</td>
</tr>
</tbody>
</table>

3.3 Sample Preparation

Commercial shape memory polymer, named styrene based Veriflex- SMP, has been obtained from Cornerstone Research Group (CRG) Inc., as thin sheet. Then the samples of desired dimension according to the test have been cut from this sheet. The geometry used for different
kinds of tests has been given in the following Table 3. After that the samples have been polished using 1200 grit sandpaper to remove surface roughness.

Table 3: Sample geometry for different kinds of tests

<table>
<thead>
<tr>
<th>Number of Tests</th>
<th>Sample Geometry (lengthxwidthxthickness) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermomechanical cycle</td>
<td>35 x 6 x 2.5</td>
</tr>
<tr>
<td>Recovery force</td>
<td>35 x 6 x 2.5</td>
</tr>
<tr>
<td>Water uptake</td>
<td>35 x 6 x 1.2</td>
</tr>
<tr>
<td>Dynamic mechanical thermal analysis</td>
<td>35 x 6 x 1.2</td>
</tr>
<tr>
<td>Stress relaxation</td>
<td>35 x 6 x 1.2</td>
</tr>
<tr>
<td>FTIR</td>
<td>20 x 11 x 3.5</td>
</tr>
</tbody>
</table>

To conduct the designed experiments various equipments have been used. A brief description of the equipments that have been used is given in the following section.

3.4 Equipments

In order to measure the effect of degradation due to water and diesel fuel such as: shape memory capability, recovery force, visco-elastic properties and change in molecular vibration the following equipments has been used:

3.4.1 Dynamic Mechanical Analyzer (DMA)

3.4.1.1 Model: DMA- 2980

Manufactured by TA instruments Dynamic Mechanical Analyzer (DMA - 2980) is an analytical instrument used to measure the physical properties, mainly visco-elastic properties of many different types of material. The specifications of DMA-2980 are given below:
3.4.1.2 Specifications of DMA Equipment (DMA-2980)

- Sample length: 50 mm (max)
- Sample width: 15 mm (max)
- Sample thickness: 5mm - 10 mm
- Loading range: 0.001N – 18 N
- Temperature range: -145°C – +600 °C
- Frequency range: 0.01Hz – 200 Hz
- Tan delta range: 0.0001 – 10

The DMA used in this research to measure the visco-elastic properties and recovery generated by the sample has been shown in Figure 14. Figure 15 shows the tensile clamp used in

![DMA-2980](image)

**Figure 14:** DMA-2980
conducting the experiment. The tensile clamp consists of two clamps: movable and fixed clamp. The lower clamp is called the fixed clamp whereas; the upper clamp is the movable clamp. The movable clamp applies sinusoidal force on the sample with the help of a variable speed motor. Due to the application of applied force, the sample undergoes sinusoidal deformation, which is not in the phase of applied force because of visco-elasticity property. From the difference in the phase angle between the applied force and the resultant deformation and using Eq. 4 the DMA could measure the visco-elastic properties of the material.

3.4.2 Rheometrics Scientific Analyzer (RSA-III)

The TA Instruments Rheometric Scientific Analyzer, RSA-III and the tensile clamp shown in Figure 16 and 17 respectively have been used in this thesis. It uses a servo linear actuator to impose an oscillatory deformation or strain, mechanically upon the material to measure the dynamic mechanical properties.
3.4.2.1 Specification of the RSA-III Equipment (RSA III)

Temperature range: -150°C to +600°C

Temperature ramp rate: 0.1°C to 50°C/min

Phase angle resolution: ± 0.1°

Frequency range: 1×10E-6 to 80 Hz

Strain resolution: ± 0.05 µ

Maximum force capacity: 35 N

Figure 16: Rheometric Scientific Analyzer (RSA-III)
3.4.3 Fourier Transform Infrared (FTIR) Spectroscopy

In order to determine the root cause of a degradation process in a polymer it is necessary to identify chemical properties of an unknown substance or contaminants. The identification becomes more challenging when the contaminant is organic in nature because of the presence of thousands of organic compounds. FTIR Spectroscopy becomes an important technique for characterizing organic materials and certain inorganic compounds. The basic principle of FTIR lies on the absorption of infrared photons, which excite vibrations of molecular bonds. The amplitude of vibrations or a rotation of chemical bonds increases at specific frequencies corresponding to discrete energy levels due to the interaction of infrared light with the matter. This frequency is related to the shape of the molecular potential energy surfaces, the masses of
the atoms, and the vibronic coupling. In this way, the presence of a functional group in a sample can be identified by the correlation of the bond wave number position with chemical structure.

The following section describes the experimental procedure that has been followed during the experiment. For each type of experiment, a specific procedure has been followed.

3.5 Experimental Method

3.5.1 Dynamic Mechanical Thermal Analysis (DMTA) Tests

To investigate the change in dynamic mechanical properties of virgin (never used before) SMP samples and the one degraded by water and diesel fuel as a function of time, DMTA tests have been performed on RSA-III, manufactured by TA instruments, in strain-controlled dynamic temperature ramp mode at a constant frequency of 1.0 Hz in the temperature range of 30°C to 100°C at a heating rate of 3°C/min. The set up of the experiment is shown in Figure 18. The tensile clamp has been used in this experiment and the gaps between the clamps are 15 mm.

![Tensile clamp](image)

Figure 18: Set up of experiment
3.5.2 Recovery Force Measurement

In order to measure the recovery force and time, a special test program has been developed. The program is a two-stage process. In the first stage, the temperature of the sample has been raised to above the glass transition temperature to accommodate deformation. Then the sample has been deformed to a set strain (50% strain). Finally, the deformed sample has been cooled down below the room temperature while keeping the strain locked-in. This stage deforms the sample into a ‘reconfigured’ state.

The aim of the second stage is to observe the recovery behavior of SMP. In this stage, the deformed sample is actuated while the machine is set to prevent strain recovery in the sample. On the Dynamical Mechanical Analyzer (DMA-2980), this test was performed in the iso-strain mode (the material is given a certain amount of constant strain and the force required to maintain that strain is measured as a function of temperature). During the strain recovery test, the temperature was ramped at 5°C/min between 30°C and 100°C. The samples were tested using tensile-clamp of the DMA testing machine.

The recovery experiments have been done on three samples and the average of the three readings has been taken in order to get consistent behavior. Also, in this experiment the recovery stress, instead of recovery force has been measured to compensate for the effect of the cross-sectional dimensions.

3.5.3 Stress Relaxation Tests

The stress relaxation properties of SMP have been determined using RSA-III (manufactured by TA instruments). In this experiment, the force required to maintain a constant tensile strain of 0.4% was monitored as a function of time, at a constant temperature of 30°C.
The set up of the sample in the equipment is the same as shown in Figure 18. The gap between the clamps was kept 15 mm, as before.

3.5.4 Fourier Transform Infrared (FTIR) Spectra

Fourier transform infrared (FTIR) spectra were obtained using an Attenuated Total Reflectance (ATR) cell covering the 650 to 4000 cm\(^{-1}\) spectral range using Bruker-Tensor 27 FTIR system. Each FTIR-ATR spectrum was the average of 64 scans at 4cm\(^{-1}\) of nominal spectra resolution, using air as reference. The FTIR data were analyzed using OPUS 6.5 data Collection Program software.
4. RESULTS AND DISCUSSION

This section focuses on the discussion of the results obtained from various tests which have been conducted to investigate the effect of degradation of Veriflex- SMP due to water and diesel fuel. The focus is placed also on correlating them with the theoretical concepts introduced here.. First, the basic properties of SMP are discussed, followed by the examination of the plasticization effects on the degradation behavior of this SMP material.

4.1 Visco-elastic Properties

The result of the ambient scan of dry SMP is shown in Figures 19 to 21. “Dry SMP” in this case is defined as the SMP that was equilibrated at the room temperature conditions.

Figure 19: The behavior of storage modulus as a function of temperature for untreated SMP
Figure 20: The behavior of loss modulus as a function of temperature for untreated SMP

Figure 21: The behavior of tan$\delta$ as a function of temperature for untreated SMP
From the behavior of storage modulus curve shown in Figure 19, we have seen that at the initial stage, the storage modulus of the polymer is $1.03 \times 10^9$ Pa which represents its load bearing capacity at room temperature whereas at high temperature, the storage modulus drops almost to zero. Macroscopically, this means that the phase angle between stress and strain approaches $90^\circ$. In another word, the energy stored by the sample per cycle of deformation becomes negligible in comparison to that energy dissipated as heat. In the transition region, the storage modulus decreases with the increase of temperature. This is expected, since at room temperature, the soft and hard segments of shape memory polymer are in glassy state. As a result, it can withstand a large amount of load. With the increase of temperature, the hard segments of shape memory polymer do not undergo any kind of change. However, the mobility of soft segments increases due to the lifting of external constraint which results in the increase of heat dissipation. As a result, the storage modulus of shape memory polymer decreases with the increase of temperature.

From Figure 20, we have seen that at the beginning with the increase of temperature, the loss modulus increases. This is because with the increase of temperature, the molecular mobility of soft segment increases which, in turn, increases the heat dissipation. After going through the maximum attainable temperature limit, the loss modulus begins to decrease and ultimately, at higher temperature it goes to zero. In terms of molecular viewpoint, this may be due to the absence of any molecular or atomic adjustments capable of dissipating energy within the period of deformation.

From the behavior of tan delta curve, which is shown in Figure 21 we have seen that in the transition zone between glasslike and rubberlike consistency, the tangent delta value goes through a pronounced maximum. This is associated with configurational rearrangement of the
strands of the network structure of the soft segment. The maximum for this type of polymer is attributable to the entanglement network, in which the entanglements suppress long-range configurational rearrangements almost as though they were cross-links.

The storage modulus, loss modulus, and tangent delta values are the three different methods to determine the transition temperature, since each property is dependent on the molecular movement of the polymer. From our results, we see that DMA spectrum of storage modulus curve of SMP shows a drop of storage modulus from \(1.03 \times 10^9\) to 0 Pa in the temperature region between +30°C and +70°C. The loss modulus and Tan δ shows peak at +50°C and +72.2°C, respectively. Usually the DSC related \(T_g\) and DMA related \(T_g\) varies within ±4°C for a variety of polymers.

According to Rosalie et al. (1996), the \(T_g\) is defined as the shift of midpoint of the heat capacity curve obtained from DSC readings. On the other hand, for DMA, the \(T_g\) is taken as the average of the \(E''\) and Tan δ peak temperatures measured at 1.0 Hz. In our case, the temperatures at peak of \(E''\) and tan δ are 50.6°C and 72.2°C respectively. Therefore, the glass transition temperature, \(T_g\) of our Veriflex-SMP, according to our test is:

\[
T_g = \frac{50.579 + 72.185}{2} \text{°C} = \frac{122.764}{2} \text{°C} = 61.382 \text{°C},
\]

which is quite close to the value 62°C supplied by the Veriflex’s manufacturer, Cornerstone Research Group. This confirms that the correctness of our experimental procedure. We can, now take the temperature at peak of tan δ as the glass transition temperature of our material for convenience.
4.2 Shape Memory Property Testing

To determine the shape memory phenomena of styrene based Veriflex- SMP, the thermo-mechanical programming cycle has been done on the specimen and the results are shown in Figure 22. The important processes are described below:

![Image of shape memory cycle](image)

**Figure 22:** Thermally driven shape memory cycle of SMP

- The specimen is heated to 100 °C, which is above the glass transition temperature, $T_g = 62^\circ$C.

- At 100 °C the specimen has been given a 50% tensile deformation by applying a tensile force on it.

- After the deformation, the temperature of the sample has been cooled below the room temperature while maintaining the load on the specimen.
• At temperature below the glass transition temperature, the load is removed and the specimen is removed from the fixture. The resulting shape is called the deformed or temporary shape. In this condition, the length of the sample has been measured.

• Then it is heated again to 100 °C, which is above the glass transition temperature, and no-constraint was imposed on the specimen to recover the original shape.

• Finally, it is cooled to room temperature and the length of the sample has been measured from which the shape memory property of the sample has been calculated.

### 4.2.1 Evaluation of Shape Memory Capability

The following results are obtained from the thermo-mechanical cycle on the specimen:

1. **Shape fixity**

   \[
   \text{Shape fixity} = \frac{\text{fixed deformation, } \varepsilon_u}{\text{total deformation, } \varepsilon_m}
   \]

   \[
   = \frac{7.355/15}{7.5/15} \times 100\% = 98.07\% \text{ (which may be considered not very desirable, rather poor shape-fixity property).}
   \]

2. **Shape recovery ratio**,  

   \[
   \text{Shape recovery ratio} = \frac{\text{deformation recovered by the sample, } \varepsilon_m - \varepsilon_p}{\text{total deformation, } \varepsilon_m}
   \]

   \[
   = \frac{7.267/15}{7.5/15} \times 100\% = 96.9\% \text{ (which may considered reasonably good shape recovery ratio)}
   \]

3. **Recovery time**  

   The time required to recover the original shape after reaching the glass transition temperature = 10s.
From the values of shape memory property we can generally conclude that styrene based Veriflex- SMP is a good quality shape memory polymer with the exception of low shape fixity property.

4.3 Recovery Force Curve (Recovery Stress vs. Temperature Curve)

The behavior of recovery force (normalized to stress value in Y-axis to avoid cross-sectional effects) generated by styrene based Veriflex- SMP is plotted in Figure. 23. The various stages of the recovery force curve are described below:

1. From a → b: the SMP has been equilibrated at room temperature to establish thermal equilibrium between the sample holder and sample.

2. From b → c: the SMP tends to increase with the increase of temperature due to thermal expansion. The set up of the equipment restricts the expansion of the sample

![Figure 23: Recovery force curve of Shape memory polymer](image-url)
by applying compressive force on it (stress-controlled condition). This has been seen by the decrease in the force.

3. From c→d: After the stage of thermal expansion, near the transition temperature, the recovery behavior of SMP dominates and the polymer tends to shrink. However, the equipment restricts the expansion of the sample by applying tensile force on the sample. As a result, the force begins to increase and continue to increase until the temperature crosses the transition period.

4. From d → : after that the force required to maintain the deformation applied to the sample becomes asymptotically constant.

From the data, the recovery stress calculated for the SMP which is 1.080 MPa, which is reasonable level of recovery stress.

4.4 Effect of Frequency on Glass Transition Temperature, Tg

The effect of the frequency of the ambient DMA scan of untreated SMP on the position of tan δ peak is shown in Figures 24 and 25. There is a shift in the tan δ peak to a higher temperature with the increase of frequency of the scan. The overall trend is the same, i.e., the glass transition temperature increases with the increase of frequency. This effect is expected since the glass transition phenomena of SMP resulted from the slippage or rearrangement of the polymeric chain. For the rearrangement of the polymeric chain to occur, a certain amount of energy is required. At higher frequency the molecular segments does not get enough time for rearrangement at a certain energy level. As a result, the large-scale molecular motions begin at a higher temperature.
**Figure 24:** Effect of frequency on the glass transition temperature of the SMP

**Figure 25:** Temperature at the peak of tan delta of SMP as a function of frequency
4.5  Effect of Degradation due to Water and Diesel Fuel

In addition to primary chemical bonds in the main polymer chain, polymeric materials contain secondary bonds. Chemical bonds between polymer chains (permanent cross-links), intermolecular van der waal’s bonds, dipole-dipole interactions, segmental attractions and other physical couplings (temporary cross-links), chain entanglements as well as cross link density, segment mobility, crystallinity, superstructure, and other morphological features – all contribute to the macroscopic mechanical properties of the material. All of the bonds may be the reaction sites in polymer degradation and various energy sources may be effective in supplying the energy necessary to break the bonds. The most important types of energy that cause polymer degradation are heat, mechanical energy, and radiation. Although the temperature is the main source for degradation polymer in terms of supplying the energy necessary for bond scission but it is not the only source. The reaction of the polymer with moisture and chemicals, which comes in contact with the polymer during service life, is also important in polymer degradation. In this thesis, the degradation of the styrene- based Veriflex- SMP due to water and diesel fuel has been examined. At first, the intensity of degradation caused by water and diesel fuel has been compared. Then the progress of degradation with time due to water and diesel respectively, for the duration of the time period of one month has been investigated.

4.5.1  Comparison of the Degradation due to Water and Diesel Fuel with Untreated Samples

As stated earlier, the effect of water and diesel fuel on styrene based Veriflex- SMP due to immersion for 1- week has been investigated and compared with respect to each other and with un-degraded samples. In this thesis, we will compare the dynamic mechanical properties, stress relaxation, and FTIR spectra.
4.5.1.1 Change in Storage Modulus

The behavior of storage modulus as a function of temperature of the untreated sample and the sample immersed in water and diesel fuel for 1 week has been shown in Figure 26.

Figure 26: Comparison of storage modulus between untreated and treated Veriflex- SMP
Table 4: Comparison of Storage modulus between untreated and treated Veriflex- SMP

<table>
<thead>
<tr>
<th>Condition of Samples</th>
<th>Storage modulus (Pa) at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Untreated</td>
<td>$1.13 \times 10^9$</td>
</tr>
<tr>
<td>2. Treated in water for 1- week</td>
<td>$1.03 \times 10^9$</td>
</tr>
<tr>
<td>3. Treated in diesel fuel for 1- week</td>
<td>$4.41 \times 10^7$</td>
</tr>
</tbody>
</table>

From the curves shown in the Figure 26 we see that the value of storage modulus, the load bearing capacity, of the material at room temperature decreases due to exposure to solvents. To get a better understanding, the variation of the values of storage modulii at room temperature with solvents have been given in Table- 4. We also observe a greater decrease in the value of storage modulus for the case of SMP degraded by diesel fuel in comparison to water. It is an indication that diesel fuel has produced more serious degradation values in the SMP samples. We found that that due to immersion in diesel fuel the storage modulus decreases by 96.1% whereas, the decrease of storage modulus due to immersion in water is around 8.85% in comparison to untreated samples. Therefore, the decrease in storage modulus with respect to untreated samples due to immersion in

i. Water: 8.85%

ii. Diesel fuel: 96.1%
4.5.1.2 Change in Glass Transition Temperature, T_g

The behavior of tangent delta as a function of temperature due to immersion in water and diesel fuel solvents for 1 week and that of the untreated one has been shown in Figure 27.

**Figure 27:** Comparison of tan delta curve between untreated and treated VERIFLEX –SMP samples
Table 5: Comparison of the temperature at the peak of tan δ between untreated and treated Veriflex- SMP samples

<table>
<thead>
<tr>
<th>Condition of the Samples</th>
<th>Temperature (°C) at the peak of tan δ curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>71.42</td>
</tr>
<tr>
<td>Treated in water for 1 week</td>
<td>70.085</td>
</tr>
<tr>
<td>Treated in diesel fuel for 1 week</td>
<td>34.111</td>
</tr>
</tbody>
</table>

Tangent delta is defined as the ratio of the loss modulus to storage modulus. In other words, it is a factor of dissipation of energy. Usually the peak of tangent delta curve is defined as the transition temperature, $T_g$ of the material. This is the temperature upon which the polymer changes its state from the brittle glassy state to the flexible rubbery state. From these curves we see that the temperature at the peak of the tangent delta, i.e., the glass transition temperature of the material decreases due to exposure to water and diesel fuel. To get a better understanding, the variation of the temperature at the peak of tangent delta with solvent has been shown in Table-5 above. We also observe that a greater decrease in the value of glass transition for the case of SMP degraded by diesel fuel in comparison to that of water. It is an indication that the molecular structure of the polymer has been greatly affected by diesel fuel at room temperature. We also calculate the percentage of decrease in $T_g$ due to immersion in water and diesel fuel respectively with respect to untreated one. We found that due to immersion in diesel fuel the $t_g$ decreases by 52.2% whereas the decrease of $t_g$ due to immersion in water is 1.3% which is much less in comparison to that of the diesel fuel. We conclude that the decrease in $T_g$ with respect to untreated sample due to immersion in:
i. Water: 1.3%

ii. Diesel Fuel: 52.2%

4.5.1.3 Normalized Force Decay Curves

When a constant strain is applied to a polymer at a constant temperature, the force required to maintain the strain decreases with time. This behavior is called stress relaxation. In another word, stress relaxation explains how polymer relaxes stress under constant strain. The stress relaxation, which depends upon the time scale, is usually the result of both physical and chemical processes.

i. Physical relaxation

Under deformation the polymer chains and the fillers rearrange themselves. This occurs within a very short span of time, right after deformation in a polymer.

ii. Chemical relaxation

If the polymer comes in contact with chemical, oxygen/air and/or subjected to heat and light, then the polymer chain breaks. Sometimes the polymer undergoes through decross-linking. As a result, the counter force during stress relaxation testing has been decreased.

For short time and/or at room temperature, usually physical processes are responsible for the cause of stress relaxation. But in degradative environments or at higher temperature and/or for long times, chemical processes are more significant than physical processes. An ideal spring will store the applied force and release it on the removal of the load. But the polymers have a tendency to relax to equilibrium condition. As a result, the chemical and physical relaxation within the polymer has been occurred.
Figure 28: Decay of stress due to immersion in water and diesel fuel

Figure 28 shows the decay of normalized force as a function of time for the untreated samples and the treated one with water and diesel fuel for one week. At the initial stage, the force required to maintain the deformation has decreased significantly. After the initial decrease of force, the force required to maintain the deformation remain almost constant with the passage of time and ultimately it reaches a plateau. The decay in force is the indicative of the onset of the physical and chemical relaxation processes within the SMP. In comparison, a perfect or ideal spring not suffering these effects will store the applied force and release the energy on removal of the load. It is also evident from Figure 28 that the rate of decay in force is greater for the degraded ones.
We can also see that due to immersion in diesel fuel the force required to maintain the deformation becomes almost zero. This is an indication of the change of state of the polymer from the glassy state to the rubbery state due to the immersion in diesel since, we know that in the rubbery state, the polymer is able to accommodate a large amount of deformation. The mechanism is attributed to the dissociation of diesel and water species to form hydronium ions. These may, in turn, attack the polar C=O backbone resulting bond scission which relieves the stress. After that, the condensation of these groups subsequently occurs in the relaxed state. This intermolecular recombination will generate a new network, especially in the presence of stress, resulting in chemical stress relaxation.

4.5.1.4 Change in Fourier Transform Infrared (FTIR) Spectra

Chemical degradation of polymer produces a complex mixture of different products. The precise identification and quantification of the degradation products is essential to understand the mechanism of degradation. FTIR is the most informative analytical technique to study the degradation of polymer.

Fourier transform infrared spectroscopy was used to follow the structural changes in the SMP during degradation. These compounds generally possess extensive hydrogen bonding systems. The possible functional groups acting as electron donors in the hydrogen bonding with the amide group are the urethane carbonyl and the pre polymer ester oxygen. In the following, we mainly concentrate on the analysis of the C=O stretching region which is regarded to be the most favorable for the characterization of hydrogen bonding in polyester, both qualitatively and quantitatively. Representative full FTIR spectra of the untreated styrene based Veriflex- SMP
Figure 29: Comparison of FTIR spectra between the treated SMP and the untreated SMP

Figure 30: FTIR spectra of styrene based Veriflex- SMP in the range of 1700 cm\(^{-1}\) to 2000 cm\(^{-1}\)
and the one treated in water and diesel for one week at the temperature of 25°C is shown in Figure 29. From the Figure 29 we can see that due to the degradation the peak intensity at several locations has been increased and shifted either to the right or to the left.

The peak of bonded C=O that is relevant to this study has been identified according to two references [Huang et al. 2005, Yen et al. 1999]. Two overlapping bands are present in the carbonyl stretching region – two dominating peak apparently at 1720 cm\(^{-1}\) and close to 1739 cm\(^{-1}\). These signals are ascribed to the stretching vibrations of non-hydrogen bonded and hydrogen bonded carbonyl respectively.

Figure 30 shows that due to immersion in water for 1 week, the peak intensity of the infrared band of free C=O stretching increases whereas the infrared band of the hydrogen bonded C=O stretching has been diminished. On the other hand, due to immersion in diesel for 1 week, the infrared band of the hydrogen bonded C=O stretching shifts slight to a lower frequency. Also, with the increase of immersion time the infrared band of the bonded C=O stretching becomes more apparent compared with that of the free C=O stretching, which indicates that a longer immersion time activates more C=O groups in hydrogen bonding.

### 4.5.2 Effect of Degradation due to Water

After comparison of the degradation due to water and diesel fuel with the undegraded one, now we investigate the effect of water on styrene based Veriflex- SMP alone with the increase of immersion time. As in the previous case, the dynamic mechanical properties, stress relaxation, and FTIR spectra have been investigated.
4.5.2.1 Shape Memory Phenomena

The thermo-mechanical cycle to investigate the shape memory phenomena of styrene based Veriflex- SMP due to immersion in water has been shown in Figure 31. The processes of the thermo-mechanical cycle have been described below:

![Figure 31: Shape memory phenomena of SMP due to immersion in water](image)

- Initially, the SMP was in brick shape, which is termed as its original shape.
- At this stage, the temperature of the SMP has been increased above the transition temperature and it has been deformed to a certain amount of tensile deformation (about 50%). After the application of deformation, the SMP has been cooled below the transition temperature while maintaining the constant load. At temperature below the transition temperature, the load has been removed. At the
glassy state, the polymer is not able to reconfigure itself and the deformation has been locked-in. This shape is known as deformed or temporary shape.

iii. The deformed shape has been immersed in distilled water for up to 12 weeks to investigate the effect of water on the shape fixing capability of SMP.

It has been shown that water does not have much effect on the shape fixing property of styrene based Veriflex- SMP. On the other hand, the color of SMP has been changed from transparent to opaque, ivory white (Fig. 31).

4.5.2.2 Change in Glass Transition Temperature

From the Figure 32 we have seen that water does not have any significant change on the glass transition temperature of styrene based Veriflex- SMP.

![Figure 32: Behavior of tan delta as a function of temperature due to immersion in water](image-url)
Table 6: Change in transition temperature due to immersion in water

<table>
<thead>
<tr>
<th>Condition of Samples</th>
<th>Temp at peak of tanδ (°C)</th>
<th>% change in T&lt;sub&gt;g&lt;/sub&gt; with respect to untreated-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated-1</td>
<td>72.185</td>
<td></td>
</tr>
<tr>
<td>Untreated-2</td>
<td>73.004</td>
<td></td>
</tr>
<tr>
<td>Treated in water for 1 week</td>
<td>71.25</td>
<td>1.3%</td>
</tr>
<tr>
<td>Treated in water for 2 weeks</td>
<td>70.927</td>
<td>1.74%</td>
</tr>
<tr>
<td>Treated in water for 3 weeks</td>
<td>69.775</td>
<td>3.33%</td>
</tr>
<tr>
<td>Treated in water for 4 weeks</td>
<td>68.824</td>
<td>4.66%</td>
</tr>
</tbody>
</table>

The percentage change in the transition temperature with respect to the untreated one has been shown in Table 6. From the table we have found that after immersion for 4 weeks the change in transition temperature is only 4.66%. Li S. (1999) have been found that the water absorbed in SMP can be divided into two groups: Free water and bound water. Free water can be removed by heating the SMP above the transition temperature whereas bound water only begins to evaporate upon reaching the transition temperature. From our experimental results we can conclude that water absorbed during four weeks to SMP at room temperature is mainly free water.
4.5.2.3 Change in Stress Relaxation

The change in stress relaxation due to immersion in water has been shown in Figure 33. It is seen that due to immersion in water, the relaxation of force occurs at a faster rate in comparison to the untreated one. It has also been found that there is no difference in stress relaxation between 1 week to 3 weeks duration of immersion time. However, for the duration of 2 weeks we see a difference in stress relaxation in comparison to 1 and 3 weeks. This may be due to experimental error. One more significant result is that after duration of immersion in water for 3 weeks the polymer does not lose its capacity to withstand the load. [Comment: expand this observation from your new experiment that you are doing now]

![Graph showing stress relaxation](image)

**Figure 33:** Decay of stress of Veriflex- SMP due to immersion in water
4.5.2.4 Change in FTIR Spectra

The changes in FTIR spectra due to immersion in water has been shown in Figure 34. From the Figure it has been seen that with the increase of duration of immersion in water the band at 1740 cm\(^{-1}\) which is attributed to hydrogen bonded C=O has been shifted to the left position. Also with the increase of immersion time the band at 1720 cm\(^{-1}\), corresponding to free C=O bonding, becomes inapparent whereas band at 1740 cm\(^{-1}\) becomes striking. This results indicate that the increase of immersion time triggers more C=O bonding into hydrogen bonded.

**Figure 34:** Change in FTIR spectra due to immersion in water
4.5.3 Effect of Diesel Fuel

After investigating the effect of water on SMP with the increase of immersion time we now turn our attention to investigate the effect of degradation on styrene based Veriflex- SMP due to diesel fuel. Here, we investigate shape memory phenomena, dynamic mechanical properties, and FTIR spectra.

4.5.3.1 Shape Memory Phenomena

We investigate the shape memory phenomena of styrene based VERIIFLEX -SMP due to immersion in diesel fuel by going through the thermo-mechanical cycle which is shown in Figure 35. The processes of the thermo-mechanical cycle have been described below:

![Figure 35: Shape memory phenomena of SMP due to immersion in diesel fuel](image)

Figure 35: Shape memory phenomena of SMP due to immersion in diesel fuel
i. Initially, the SMP was in brick shape, which is termed as its original shape.

ii. At this stage, the temperature of the SMP has been increased above the transition temperature and it has been deformed to a certain amount of deformation (about 50%). After the application of deformation, the SMP has been cooled below the transition temperature while maintaining the constant load. At temperature below the transition temperature, the load has been removed. At the glassy state, the polymer is not able to reconFigure itself and the deformation has been locked-in. This shape is known as deformed or temporary shape.

iii. The deformed shape has been immersed in diesel fuel to investigate the effect of diesel fuel on the shape fixing capability of SMP.

It is observed that due to immersion in diesel at room temperature, styrene based Veriflex-SMP has been recovered its original shape after two weeks. The shape recovery of the SMP is almost 99%. It indicates that diesel fuel has a great influence on the shape fixing property of styrene based Veriflex- SMP. On the other hand, the color of SMP has been changed from transparent to opaque, yellowish (fig. 35).

4.5.3.2 Change in Transition Temperature

The effect of diesel fuel on the glass transition temperature, $T_g$ of Veriflex- SMP is shown in Figure 36. It is seen that due to the immersion in diesel fuel for 1 week, the transition temperature of SMP has decreased to 34°C whereas due to immersion for 2 weeks, the transition temperature goes below the room temperature. The findings exactly verify the result obtained from thermo-mechanical cycle. It has also been observed that there is a considerable fluctuation in the behavior of tan $\delta$ curve, which also indicates that the material goes into the rubbery state.
As a result, the material is not able to withstand any amount of load and the fluctuations arrived from the frequency of the equipment.

Figure 36: Change in transition temperature due to immersion in diesel fuel

4.5.3.3 Change in Stress Relaxation

The effect of diesel fuel in stress relaxation of styrene based Veriflex- SMP is shown in Figure 37. It is shown that due to the immersion in diesel fuel even for 1 week the stress relaxes
drastically and ultimately it goes to zero. From the results, we can conclude that due to immersion in diesel fuel the Veriflex- SMP has gone to rubbery state since its load retention capacity goes to zero. We can also conclude that besides physical process, chemical process also occurs during the immersion period of SMP into diesel fuel, which breaks the crystalline portion of soft segment completely.

![Graph: Decay of stress of Veriflex- SMP due to immersion in diesel fuel](image)

**Figure 37:** Decay of stress of Veriflex- SMP due to immersion in diesel fuel
4.5.3.4 Change in FTIR Spectra

The changes in FTIR spectra of styrene based Veriflex- SMP is shown in Figure 38 in the ranges from 1700 cm\(^{-1}\) to 1780 cm\(^{-1}\). From the Figure 38 it is shown that due to the increase of immersion time in diesel fuel the band at 1740 cm\(^{-1}\) which has been attributed to the hydrogen bonded C=O has been shifted to the left. From this result, we can conclude that the increase of immersion time triggers more C=O bonding into hydrogen bonding.

\[\text{Figure 38: Changes in FTIR spectra due to immersion in diesel fuel}\]

been attributed to the hydrogen bonded C=O has been shifted to the left. From this result, we can conclude that the increase of immersion time triggers more C=O bonding into hydrogen bonding.
4.6 Discussion

Shape memory polymer consists of hard and soft phases, which are incompatible. The hard and soft phases are randomly distributed along the polymer chain forming a structure of separated micro-phases. These phases can be of different shapes and sizes. The arrangement of the hard segments can vary from non-ordered arrangement to an ordered arrangement along the main polymer chain. Similarly, the soft phase can be amorphous or crystalline in structure.

According to Huang et al. (2005) the water absorbed in SMP can be divided into two groups: free water and bound water. Free water does not have any effect on the glass transition temperature and it can be removed by heating above the transition temperature. On the other hand, the bound water has a pronounced effect on the glass transition temperature. Due to this behavior, the glass transition temperature has been decreased and it cannot be removed by heating it above the transition temperature rather it starts to evaporate at the transition temperature. The plasticization effects of water and diesel fuel also have a significant influence on the deterioration of property of SMP. Plasticizers are low molecular weight compound due to which the rigid polymeric materials become soften. They penetrate into the polymeric matrix and interrupt the chain-to-chain secondary bonding. The mobility of the polymeric chain and free volume increases. As a result, the glass transition temperature of the material decreases. Usually, the $T_g$ of a polymer, in contact with a plasticizer, depends on the $T_g$ of the plasticizer. In this thesis, the $T_g$ of the solvents used, water and diesel fuel, is much below in comparison to that of Veriflex- Shape Memory Polymer, $62^\circ$C, and acts as a good plasticizer. As a result, the mechanical property of shape memory polymer has been degraded because of the plasticization effect of both solvent. From the stress relaxation test we see that due to immersion in water the load bearing capacity of shape memory polymer has been decreased. We also see that diesel fuel
acts as a better plasticizer for shape memory polymer in comparison to water since the load bearing capacity of shape memory polymer goes to almost zero due to immersion in diesel fuel.

From molecular point of view, it has been well established that the degradation mechanism of polyesters are hydrolytic process. Due to the cleavage of an ester bond by water produces a carboxyl end group and a hydroxyl one. The carboxyl end group thus formed is able to catalyze the other ester bonds [Li S., 1998]. It is known that the degradation of polymer in aqueous media consists of two stages. At the first stage, water penetrates into the amorphous region with random hydrolytic scission of ester bonds. After the degradation of the amorphous region, the water molecule begins to attack the crystalline domain, which consists of the second stage.

### 4.7 References


5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

The main aim of this thesis is to study the effects of degradation due to water and diesel fuel on the properties of styrene based Veriflex-SMP. In the course of this work, visco-elastic properties, stress relaxation, and structural integrity, the crucial factors in the design and selection of SMP for sealing application were also investigated. The changes in the structural integrity of the materials were related to the changes in the physical properties of the SMP as a function of degradation. The general key conclusions of the study are summarized below:

- The degradation behavior of Veriflex- SMP due to two types of solvents, water and diesel fuel, have been analyzed.
- Veriflex- SMP immersed in water and diesel, showed the similar tendency in terms of degradation of property.
- The chemical degradation of Veriflex- SMP in the above mentioned two environments was also evaluated.
- Due to immersion in diesel fuel, the appearance of Veriflex- SMP changes from transparent to opaque, yellowish one. On the other hand, due to immersion in water, the appearance of Veriflex- SMP changes to ivory white.
- Due to degradation by diesel fuel significant reduction in glass transition temperature has been achieved; whereas the change due to degradation by water is less significant.
- It is found that the Veriflex- SMP is able to recover the original shape from the deformed shape upon immersion in diesel fuel for 2 weeks; but the extent of recovery depends on
the thickness of the sample. Thus, shape recovery of Veriflex- SMP can be triggered not only by applying energy but also without energy.

- Micro molecular solution absorbed in the Veriflex- SMP weakens the elasticity modulus, which causes a significant decrease in the $T_g$. As a result, the SMP is able to recover the original shape. This tendency of decrease in the value of $T_g$ has been found by DMA tests.
- It has been found that hydrogen bonding is mainly responsible for the changes in properties of Veriflex- SMP.

5.2 Recommendations for Future Work

This thesis has left many question unanswered and a range of experiments can be conducted in order to prove unequivocally some of the ideas presented in this work and to clarify others.

- If we want to use Veriflex- SMP as a structural member then there is every possibility that in most applications, it will be subjected to a large amount of deformation. The stress relaxation experiments of this thesis have been conducted for a small amount of strain. The stress relaxation experiments can be conducted for a large amount of strain. In order to accomplish this, one will need to build up a experimental set-up. The experimental set-up should be able to apply a large amount of deformation on the sample while at the same time, allowing the operator to measure the force to maintain the deformation as a function of time.
- In this thesis, at first, the samples are immersed in water and diesel fuel respectively, and then experiments have been conducted. A new method of experiment can be designed to perform the experiment while undergoing continuous degradation process. In another
way, the experimental set-up should allow the operator to monitor the change in force, to maintain the certain level of deformation, as a function of time while the sample is being immersed in diesel fuel or water.

- In this thesis, the recovery force generated by untreated SMP has been calculated. From the findings of this thesis, it is certain that due to degradation by water and diesel fuel, the recovery force generated by Veriflex- SMP will change. The change in recovery force due to degradation can be investigated.
VITA

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