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SHAPE MEMORY POLYURETHANE BASED ON PALM OIL POLYOL

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Shape Memory Polyurethane Based on Palm Oil Polyol”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATIONS

BD	1,4- Butanediol
DBTDL	Dibutyltin dilaurate
DSC	Differential Scanning Calorimeter
FTIR	Fourier-Transform Infrared Spectroscopy
MDI	4,4- Diphenylmethane diisocyanate
PCL	Polycaprolactonediol
POP	Palm oil polyol
PU	Polyurethane
RT	Room temperature
SMA _s	Shape memory alloys
SMC _s	Shape memory ceramics
SME	Shape memory effect
SMH	Shape memory hybrid
SMM	Shape memory material
SMP _s	Shape memory polymers
SMPU	Shape memory polyurethane
SWNT	Single-wall carbon nanotubes
TGA	Thermogravimetric Analysis
XRD	X-ray diffraction
-OH	Hydrogen bonding
-NCO	isocyanate group
H-NH	Hydrogen bonded amine
F-CO	Free carbonyl bonding

H-CO

Hydrogen bonded carconyl

LIST OF SYMBOLS

mm	Millimeter
cm	Centimeter
μm	Micrometer
$^{\circ}\text{C}$	Degree Celsius
%	Percentage
ΔH	Heat of fusion
T_g	Glass transition temperature
T_m	Melting temperature
T_{trans}	Transition temperature
θ	Angle
λ	Wavelength

POLIURETANA MEMORI BENTUK BERASASKAN POLIOL MINYAK KELAPA SAWIT

ABSTRAK

Dalam kajian ini, poliuretana memori bentuk (SMPU) telah dihasilkan dengan menggunakan polioliol berasaskan minyak kelapa sawit (POP) bagi mengurangkan penggunaan polioliol berasaskan petroleum. Pertambahan POP yang digunakan adalah sebanyak 20% dan tempoh tindak balas bagi sintesis prepolimer adalah dari 2.5 hingga 5 jam. SMPU berasaskan POP telah dihasilkan menggunakan proses pempolimeran dua-peringkat. Kesan penambahan POP dan masa tindak balas dapat di kaji berdasarkan analisa sifat terma, mekanik dan sifat memori bentuk. Kehabluran SMPU didapati berkurang dengan penambahan kandungan POP disebabkan oleh pembentukan lebih banyak segmen keras yang menghalang proses penghabluran kristal PCL. Walau bagaimanapun, kehadiran struktur berhablur masih mencukupi untuk menunjukkan sifat ketetapan bentuk yang efisien bagi SMPU sehingga 20% nisbah molar POP. Walaupun sifat pemulihan tidak menunjukkan 100% pemulihan tetapi ia boleh diklasifikasikan sebagai bagus kerana sifat pemulihan sampel hampir 100%. Sifat mekanik juga berubah dengan kehadiran POP dan nilai maksimum didapati pada 10% nisbah molar POP. Sifat mekanik bagi kajian terhadap tempoh tindak balas pula menunjukkan nilai paling maksimum adalah pada 4.5 jam bagi kedua-dua kumpulan nisbah molar, 10% dan 20% POP. Sebaliknya, sifat hablur pula menunjukkan nilai minimum pada waktu 4.5 jam. Keputusan dari kajian ini, SMPU berasaskan 10% POP menunjukkan peningkatan dalam sifat terma, mekanik dan memori bentuk berbanding SMPU tulen. Begitu juga dengan peningkatan masa tindak balas bagi POP yang juga menunjukkan peningkatan terhadap sifat- sifat di atas pada masa 4.5 jam.

SHAPE MEMORY POLYURETHANE BASED ON PALM OIL POLYOL

ABSTRACT

In this study, shape memory polyurethane (SMPU) was prepared based on palm oil polyol (POP) to reduce the usage of petrochemical based polyol. The amount of POP used was up to 20% and the total reaction time for prepolymer preparation was 2.5 to 5 hours. POP based SMPU was prepared via two-step polymerization process. The effect of POP addition and reaction time of POP were investigated using thermal analysis, mechanical and shape memory properties. The crystallinity of SMPU decreased with addition of POP due to the formation of hard segments that restrict the crystallization of PCL crystals. However, the presence of crystalline structure was still sufficient to exhibit excellent shape fixity up to 20% molar ratio of POP content. Even though the shape recovery does not achieved 100% recovery, it can be classified as a good recovery because it was recovered almost to 100%. It was also found that the mechanical properties were changed with addition of more POP content and that the maximum values were obtained at 10% molar ratio POP based SMPU. The mechanical properties based on reaction time also showed maximum value at 4.5 hours for both 10% and 20% molar ratio of POP. Meanwhile, the reaction time at 4.5 hours showed minimum value of crystallinity for both molar ratios. Based on this study, the SMPU based on 10% POP showed improved thermal, mechanical and shape memory properties compared to pure SMPU. The reaction time at 4.5 hours also showed an excellent result toward the thermal, mechanical and shape memory properties.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Shape-memory material are those materials that have the ability to memorize a macroscopic (permanent) shape, be manipulated and fixed to a temporary and form a shape under specific conditions of temperature and stress, and then later it will relax to the original, stress-free condition under thermal, electrical, or environmental command. This relaxation is associated with elastic deformation stored during prior manipulation (Liu et al., 2002). In the past few years, there were many researches done on shape memory materials, including shape memory alloys (SMAs), shape memory ceramics (SMCs), shape memory polymers (SMPs), and the latest is shape memory hybrid (SMH).

Shape memory polymers (SMPs) are one of the shape memory materials that have gained widespread attention in both industrial and academic fields due to lightweight, low cost, easy processing, and high shape recovery strain, in the order of 100% as compared to other shape memory materials. The shape memory polymer is first conventionally processed to receive its permanent shape. Afterwards, it is deformed at a temperature above its transition temperature (T_{trans}), and then quickly cooled down to fix a temporary shape. The permanent shape is recovered by reheating the specimen above T_{trans} . Cooling down the polymer below T_{trans} again does not cause a macroscopic shape change. The effect described above is called shape memory effect.

Besides that, in order to perform the mechanical functions of fixing and recovery of deformation, the shape memory polymers typically contain two phases, fixed phase and reversible phase. The fixed phase is responsible for the permanent shape, may be composed of chemically cross-linked domains or crystals with higher phase-transition temperature, so that the domains associated with the fixed phase provides stiffness to the material at temperature T_{trans} . On the other hand, the reversible phase maintains the temporary shape and thereby serves as a molecular switch. The transition temperature of the reversible phase can be either a glass transition, T_g or a melting temperature, T_m (Cao, 2008). Figure 1.1 shows the processing for behavior of shape memory polymers.

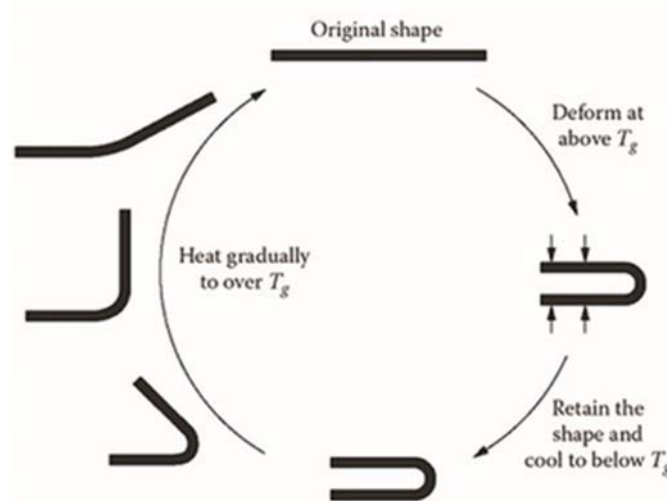


Figure 1. 1: Process occur in shape memory polymers, SMPs (Cao, 2008)

The first shape memory polymer used in the industry started in early 1950s designed by Paul Cook in the production of heat shrinkable tubing using polyethylene. Then, around the year of 1990s shape memory polyurethane was introduced by Mitsubishi Heavy Industry Ltd. After that, the study of shape memory polyurethane is more intensified by other researchers in order to improve the final properties of the

polymer by using polyurethane as a basic material. Gu and Mather (2012) produced the shape memory polyurethane composed of physical crosslinking to retain its original shape.

Polyurethane is one of polymer that has a shape memory property. PU can be found in many forms such as adhesive, foam, coating, elastomers etc. and it covers a wide range of applications from household appliances to aircraft parts owing to its versatility characteristics. The most advanced application of polyurethane is in the field of intelligence or smart materials as shape memory polymer. The shape memory polyurethane has the ability of changing shape upon application of an external stimulus. The shape memory effect is induced due to the existence of two separated phases of polyurethane owing to the non-homogeneity of soft and hard segment domains (Ali et al., 2012). One of the earliest usages of the shape memory polyurethane is fork and spoon for arthritis patients. It is also widely used in medical field and example of commercial-based products is catheters, urinary tube, intravenous cannula and etc. This product is commonly used in surgery and now is still being studied to improve the performance and usefulness (Jung and Cho, 2010). There are also research on automotive part based on shape memory polyurethane such as airflow control system in vehicle (Leng et al., 2009).

Most of the previous studies focused on the usage of petroleum as a raw material to produce shape memory polyurethane (SMPU). There are also studies conducted on preparing SMPU based on natural oils such as castor, soybean, mesua ferrea, linseed oils and etc. Meanwhile, in this study, a natural resource which is palm oil polyol (POP) is used to produce shape memory polyurethane. The main purpose of using POP in this study is to reduce the usage of petroleum-based resources because it is very limited nowadays. Therefore, in order to improve the properties of polyurethane

as a shape memory materials, a renewable resource which is palm oil polyol is introduced due to its easy availability, biodegradable, low cost and environmental friendly. On top of that, the call for environmental preservation and awareness had urged the use of palm oil polyol as it is totally environmental friendly(Ali et al., 2012).

1.2 Problem Statement

Nowadays, the use of natural oils in the production of shape memory polyurethane has started to attract attention among researchers as an effort to reduce the usage of petroleum based polyol. This is because the petroleum based polyols are high in price and has few concern towards the environment. Therefore, natural oils have become the most popular alternative choice in order to overcome the environmental and price controlling issues related to petroleum industry (Fan et al., 2012). In addition, the commercial utilization of biodegradable polymers has become an active research area during past decades due to potential advantages as compared to synthetic petroleum polymers owing to their biodegradable properties (Xu et al., 2002).

Shape memory polyurethane is a smart polymer that can be deformed from permanent to a temporary shape above its transition temperature (T_{trans}). Upon reheating above the T_{trans} , the SMPU will spontaneously return to its permanent shape. In previous research works, SMPU shows high deformability, but the recovery stresses are very low, thus limiting the size of the components (Ivens et al., 2011). Therefore, there is a need for further investigation to improve the properties of shape memory polyurethane. Most of the previous research works were focusing on castor oil based SMPU since there is no further processing required to attach hydroxyl functional groups since castor oil is composed of naturally occurring hydroxyl groups in its

structure. However, there were also other research studies focusing on preparation of SMPU based on soybean oil, linseed oil, sunflower oil and other type of natural oils in order to further improve the properties of SMPU.

However, to the best of our knowledge, there were only few studies done in the production of shape memory polyurethane based on palm oil polyol (POP). Therefore, in this study, an effort was made to produce shape memory polyurethane based on palm oil polyol to replace part of the polyol based on petrochemical. POP is useful due to its low cost, biodegradable and easy availability as compared to petroleum based polyol which is more limited nowadays. The effect of substituting POP in shape memory polyurethane on the final properties of the polymer such as thermal properties, mechanical and shape memory behavior are investigated. Besides that, the reaction time of the prepolymer synthesis process also being studied in order to investigate its effect towards the properties of SMPU.

1.3 Objective

The objectives of the research are:

1. To synthesize palm oil polyol based SMPU via bulk polymerization.
2. To investigate the effect of various prepolymer reaction time on the properties of produced SMPU.
3. To characterize the produced POP based SMPU using FTIR, DSC, TGA, XRD, mechanical and shape memory testing.

1.4 Scope of Study

The aim of the present study is on the synthesis of shape memory polyurethane based on palm oil polyol via bulk polymerization process. The study aims to reduce the usage of petrochemical based polyol in SMPU by substituting with palm oil polyol in prepolymer synthesis in order to produce SMPU based on palm oil polyol. This is because POP can enhance the properties of shape memory polymer and at the same time it can reduce the cost of SMPU production due to the utilization of low cost of POP. The amount of POP used in SMPU production is from 10 % to 20 % and it is substituted in place of PCL portion during synthesis prepolymer.

Besides that, the reaction time of prepolymer during synthesis is varied in order to study its effect towards the properties of SMPU. In this study, the reaction time is varied from 2.5 hours to 5 hours of total prepolymer synthesis. Then, the SMPU samples undergo various characterization in order to investigate the properties of resulting SMPU. The presence of various content of palm oil polyol and the reaction time taken are characterized X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The thermal property of shape memory polyurethane is determined by using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC).

The tensile testing is also investigated using the Instron Universal Testing machine. On the other hand, shape memory testing was done to determine the shape memory effects of the resulting shape memory polyurethane. This is the most important testing in this study since the behavior of shape memory polyurethane can be determined by this testing. It is determined by calculating the percentage of shape fixity and shape recovery of the samples.

CHAPTER 2

LITERATURE REVIEW

2.1 Shape Memory Effect

2.1.1 History of Shape Memory Effect

Shape memory materials (SMMs) are stimuli-responsive materials that they have the capability of changing their shape upon application of an external stimulus. SMMs are featured with the ability to recover their original shape from a significant and seemingly plastic deformation when a particular load is applied. Changes in shape caused by a change in temperature are known as thermally induced shape-memory effect. The shape memory effect is widely used for long ago due to their good properties for many applications. This material is able to memorize the original shape and it will return into their original shape when the load is released. The first research about the shape memory effect is by Arne Olander which is the first observed these unusual properties in 1938 (Oksuta and Wayman, 1998), but not until the 1960's were any serious research advances made in the field of shape memory alloys (Rafique, 2011).

Nowadays, these fields have become interested to many researchers due to the applications of shape memory materials in our technology such as in aerospace, medicals, and engineering field. Besides the shape memory alloy, there are many other types of shape memory materials that has been studied by the researcher at the present time such as shape memory polymers, shape memory ceramics and newly shape

memory material which is a shape memory hybrid. These materials also can show their properties of shape memory effect same as shape memory alloy.

2.1.2 Types of Shape Memory

2.1.2.1 Shape Memory Alloy

Despite the fact that the shape memory effect, (SME) had been found as early as 1932 in AuCd alloy by Swedish researcher Arne Orlander, this phenomenon was apparently not attractive enough until the year of 1961, another discovery occurred when significant recoverable strain was observed in a NiTi alloy with a group lead by William Beuhler at the Naval Ordnance Laboratories, USA (Khan, 2008).

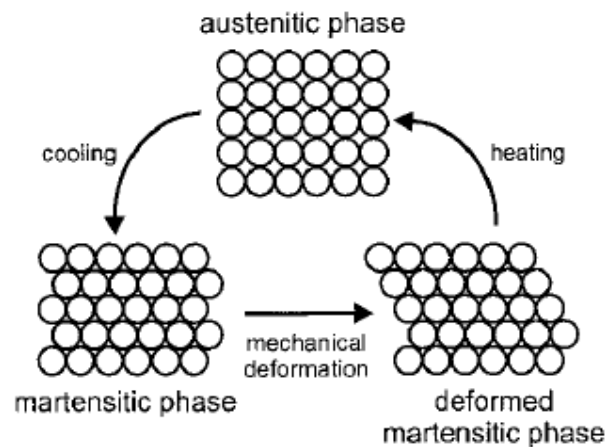


Figure 2. 1: Mechanism of the shape memory effect for metallic alloys based on a martensitic phase transformation (Lendlein and Kelch, 2002)

The shape-memory effect for alloy is based on a martensitic phase transition taking place without diffusion as shown in Figure 2.1. Based on the figure above, to perform the martensitic phase the material is cooled from high temperature or austenitic

phase to a low temperature phase. The temporary shape of the material can be produced by deformation of the material in the martensitic phase. The austenitic phase is reached upon heating the sample above the phase transition temperature and a recovery of the original external shape for deformations of up to 8% can be observed (Lendlein and Kelch, 2002).

In recent years, good progress has been made in developing ferromagnetic SMAs, which are magneto-responsive. However, a thermo-responsive SMA has matured more from the real engineering application point of view and many commercial applications have been realized. With the current trend toward micro-electro-mechanical systems (MEMS) and even nano-electro-mechanical systems (NEMS), thin film SMAs which is normally NiTi based have become a promising candidate for motion generation in these micron/ submicron systems. This is further supported by the finding of SME in nano sized SMAs and a laser beam can be used for local annealing and/or controllable growth of SMA thin films.

In addition to the SME, some of the SMAs also have the temperature memory effect (TME), so that the highest temperature in the previous heating process within the transition range can be recorded and precisely revealed in the next heating process (Sun et al., 2010). Partially different martensite after a thermal programming process is believed to be the underlying mechanism for the TME. Based on the same principle, a piece of SMA strip can be thermo-mechanically programmed to bend forward and then backward upon heating. This is a kind of phenomenon, known as the multi-SME, in which a piece of SMM recovers its original shape in a step-by-step manner through one or a few intermediate shapes (Xie, 2010).

2.1.2.2 Shape Memory Polymer

From the engineering aspect, tailoring the material properties of polymers is much easier as compared to that of metals/alloys. In addition, the cost which includes material cost and processing cost of polymers is traditionally much lower as compared to other materials. SMP materials are much lighter, have much higher recoverable strain than SMAs, and can be triggered for shape recovery by various stimuli and even multiple stimuli simultaneously (Huang et al., 2010). Furthermore, many SMPs are naturally biocompatible and even biodegradable. The thermoplastic polyurethane SMP originally invented by Dr. S. Hayashi at Nagoya R&D Center of Mitsubishi Heavy Industry, Japan has been successfully marketed for over 15 years (Hayashi, 1990). The same SMP has been developed into open-cell foams for space missions and biomedical applications based on the concept of cold hibernated elastic memory (CHEM) proposed by Dr. W. Sokolowski at Jet Propulsion Laboratory, USA (Sokolowski and Tan, 2007).

The mechanism for SME in SMPs is the dual segment/domain system which is a hard/elastic segment, while the other one can be soft/ductile segment or stiff depending on whether a right stimulus is presented. The former is called the elastic segment, and the latter is the transition segment. The SMP is normally much softer at a higher temperature than that at low temperature. This mechanism is different from the reversible martensitic transformation from shape memory alloy, which is well-known and highly predicable (Behl and Lendlein, 2010), between the high temperature austenite phase (which is hard and stiff) and low temperature martensite phase (which is soft and flexible) for SMAs.

As SMPs have a much higher recoverable strain and normally a wider shape recovery temperature range, it is possible to have more than one intermediate shape in

the multi-SME through a proper programming procedure as recently demonstrated by Xie and co-workers (2010). This proved that during constrained recovery (heating of the temporary shape of SMP), the maximum reaction force should appear as the temperature that the SMP is deformed, which means should be within the transition temperature range according to Xie. This feature reveals the TME in SMPs. The mechanism behind this feature is the step-by-step release of the elastic energy stored in the elastic segment during programming, which is different from that of SMAs.

Alternatively, the multi-SME in SMPs can be achieved by means of setting different shape recovery conditions, e.g., different stimuli or multiple transitions within different temperature ranges and even a gradient transition temperature. As such, programmed recovery in a well controllable fashion can be realized. SMP composites have remarkably widened the potential applications of SMPs. On the other hand, the shape recovery of SMPs can be accompanied with color change, excellent transparency, reversible adhesion/ peeling and even for self-healing. Similar to SMAs, the SME has been demonstrated in submicron sized SMP (Xiao et al., 2010). While it is difficult to fabricate high quality porous SMAs till now, it is always easy to produce SMP foams by many conventional polymer foaming techniques. As reported by Tey et al. (2001), complete shape recovery is observed in a 94% pre-compressed polyurethane SMP foam even after a couple of months of storage.

2.1.2.3 Shape Memory Ceramic

The mechanisms of shape memory ceramic involve the martensitic phase of ceramics. With certain ZrO₂ ceramics, the transition from a tetragonal to a monoclinic structure occurs as a martensitic phase transition which is induced thermally or by the

application of stress to form a temporary shape. The transformation back from the monoclinic to the tetragonal symmetry can occur thermo elastically, which is why martensitic ceramics show a thermo responsive shape-memory effect and return into its original shape (Lai et al., 2013).

Shape memory materials are a class of smart materials that are able to convert heat into mechanical strain or vice versa by virtue of a martensitic phase transformation. Some brittle materials such as intermetallics and ceramics exhibit a martensitic transformation, but fail by cracking at low strains and after only a few applied strain cycles. A shape memory effect also shows that such failure can be suppressed in normally brittle martensitic ceramics by providing a fine-scale structure with few crystal grains. Such oligocrystalline structures reduce internal mismatch stresses during the martensitic transformation and lead to robust shape memory ceramics that are capable of many super elastic cycles up to large strains. Shape memory ceramics with these properties represent a new class of actuators or smart materials with a set of properties that include high energy output, high energy damping, and high-temperature usage (Lai et al., 2013). Besides that, shape memory ceramics are a unique family of shape memory materials with many potential applications in sensing, actuation, and mechanical energy damping. As compared to metallic shape memory alloys (SMAs), shape memory ceramics offer many advantages such as high operating temperature, high strength and chemical inertness (Du et al., 2015).

2.1.2.4 Shape Memory Hybrid

Shape memory hybrid (SMH) is also one of shape memory materials and has their own behavior. It is a more accessible and flexible approach for ordinary people, even with

only limited scientific/engineering background. SMHs are made of conventional materials (properties are well-known and/or can be easily found, but all without the SME as an individual). Hence, one can design an SMM in a do-it-yourself (DIY) manner to achieve the required function in a particular application (Huang et al., 2010).

Similar to SMPs, SMHs are also based on the dual-domain system, in which one is always elastic (the elastic domain), while the other (the transition domain) is able to change its stiffness remarkably if a right stimulus is presented. However, the selection of the transition domains for SMHs must follow the principle that any possible chemical interaction between the elastic domain and transition domain should be minimized, if impossible to be fully avoided. This is even simpler than the hybrid organic-inorganic moiety system studied by Knight et al. (2009). As such, we can precisely predict the thermo mechanical response of an SMH based on the material properties of these two domains and the advantages of SMHs is apparent. For instance, the elastic domain can be selected to meet the requirements on the stiffness and amount of shape recovery ratio of an SMH, while the required type of stimulus can be realized by selecting a right material for the transition domain.

Furthermore, the fabrication/synthesis process is based on the well-known properties of the materials for the domains, which is straightforward. Thus, it is manageable by almost anyone even without very much experience. All features found in conventional SMAs and SMPs, namely, dual-SME, triple-SME, two-way reversible SME, a thermo-responsive, thermo/moisture-responsive, and etc. have been reproduced. A narrow shape recovery temperature range within 5°C has been achieved. This concept has been further extended into the design of pressure-responsive SMH, thermo (upon cooling or at extremely high temperature)-responsive SMH with some success (Knight et al., 2009).

2.2 Shape Memory Polymer

2.2.1 Introduction

To the best of our knowledge, the first publication regarding “shape memory” effects in polymers is based on United States patent by L. B. Vernon in 1941, who claimed a dental material made of methacrylic acid ester resin as having “elastic memory” that could resume its original shape upon heating. These shape-memory polymers (SMPs) undergo significant macroscopic deformation upon the application of an external stimulus such as heat, electricity, light, magnetism, moisture and even a change in pH value. They have been widely researched since 1980s and are an example of a promising smart material (Leng et al., 2011).

This study only focus on the shape memory polymer in which their property is better and easier as compared to other shape memory materials and finds greater popularity for its application. Shape-memory polymers (SMPs) have attracted significant attention from both industrial and academic researchers due to their fascinating functionality and applications such as temperature sensor, smart films for packaging, light responsive materials, and multifunctional SMPs. Besides these, there is a very promising field of biomedicine applications, in which SMPs can enable to be used in this technology for future applications (Sokolowski et al., 2007). One of the most notable works is biodegradable SMPs, involving implants, drug-delivery system and smart sutures. SMPs are stimuli-responsive “smart” polymers that have the dual-shape capability, which depends on the application of an external stimulus. First, SMP is conventionally processed to receive its permanent shape. Afterwards, the polymer is deformed and the intended temporary shape is fixed. This process is called programming. Finally, the permanent shape is now restored while SMP goes through

the recovery process. A change in shape caused by a change in temperature is called a thermally induced shape memory effect (SME), which is the most common method for inducing SME.

Currently, approaches for surgical medical devices, many of which are polymeric in nature, often require complex surgery followed by device implantation. But with the help of SMP, there is possibility to prepare biocompatible/degradable SMPs with appropriate mechanical properties that might enable the development of novel types of medical devices. In the research by Professor Subbu Venkatraman and his group, a biodegradable implant made by SMP loaded with therapeutic agent could be compressed and delivered inside the body, still in its compact form, via minimally invasive surgery. Once the implant is placed in the targeted site, it can be simultaneously recovered to its larger primary shape (triggered by body heat or other means) and one or more drugs can be released from the SMP matrix (Wong et al., 2014).

2.2.2 Mechanism of Shape Memory Polymer

Shape memory polymers are a class of smart materials that experience shape recoverability from state of higher strain value. The underlying mechanisms of shape memory effect are discussed in this chapter. Lower stiffness than shape memory alloys, lower mechanical strength and shape recovery stress narrow their applications, but the wholesome attribute of recoverability from a large strain make shape memory polymers attractive for many challenging applications.

Shape memory polymers also have an ability to stay in temporary shape when it was heating over the T_{trans} and immediately cooled with an applied load. Then, it can be

returned into its original shape again after reheating. T_{trans} is a temperature control of producing shape memory effects while the chain network acts as a switch of molecules. The movement of the chain is very flexible when the temperature is over the T_{trans} and high deformation occurs in the polymer chain. When the temperature is below T_{trans} , the chain movement is limited. T_{trans} of polymers are depending on network chain which may be crystalline or amorphous. Therefore, T_{trans} can become melting temperature, T_m or glass transition temperature, T_g .

In the case if the thermal transition chosen for the fixation of the temporary shape is a melting point, strain-induced crystallization of the switching segment can be initiated by cooling the material which has been stretched above the T_{trans} value. The crystallization achieved is always incomplete, which means that a certain amount of the chains remains amorphous. The crystallites formed to prevent the segments from immediately reforming the coil-like structure and from spontaneously recovering the permanent shape that is defined by the netpoints (Lendlein and Kelch, 2002). This phenomenon of temporary form and recovering the permanent shape is demonstrated schematically in Figure 2.2. Meanwhile, the phenomenon of glass transition is when the polymer is heated up over T_g , the network chains are free to move and deformation of molecules can happen. However, the cooling process below than T_g can cause the movement of molecules is in rigid and in glass form. This case can make the polymer enables for the retention of temporary form (Hu, 2007). Reheating of polymer will enable the movement of network chains again and can recover into their original shape.

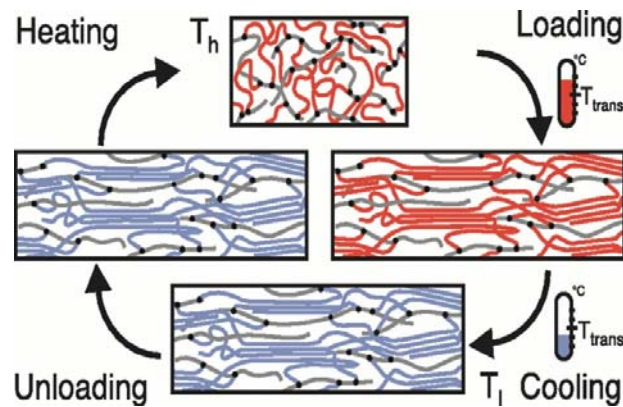


Figure 2. 2: Schematic mechanism of the thermally induced shape-memory effect

(Lendlein and Kelch, 2002)

In glassy state, the polymer chains are frozen and molecular motions are restricted to segmental and short-range conformational movements in the amorphous phase. When thermally activated by heating, a transition from glassy to rubbery-elastic state occurs, whereby backbone chain movements are dramatically increased. This enables the polymer chains to randomly distribute in the matrix. In this rubbery-elastic state, a polymer can be stretched by the application of an external force. If the uniaxial tensile stress is applied for a short period of time, the entanglement of polymer chains prevents a large scale movement of chains, resulting in storage of entropic energy and subsequent recovery of the original shape upon release of the external force. However, if the stress is applied over a longer period of time, relaxation process can take over, thus causing chain slippage and even bulk flow of polymer chains. Consequently, such deformation is irreversible. The irreversible deformation in shape memory polymers is stopped by creating cross-linked polymer chains, which act as “permanent entanglements” and prevent chain slippage. The cross-links can either be chemical or physical, or both. The size of chemically crosslinked polymer is fixed during crosslinking and cannot be changed afterwards. However, the physically cross-linked

segments, usually found in thermoplastic polymer can be deformed again at a temperature above its highest thermal transition temperature (Cao, 2008).

2.3 Shape Memory Polyurethane

Polyurethanes, PU are block copolymers containing segments of low molecular weight polyester or polyether bonded to a urethane group (-NHCO-O). Polyurethane can show the properties of shape memory effects due to its morphology, which has a phase separation segment of morphology, soft segment and hard segment. Soft segment produces a long network chain of polyol with flexibility to stand the temporary shape while the hard segment is to maintain its permanent or original shape. The differences between shape memory polyurethane (SMPU) and ordinary polyurethane can be seen by the presence of two separation morphology in their molecule chain (Ji et al., 2007).

The shape memory effect of segmented polyurethane is due to the network structure formed by hard and soft segment. The deformations of SMPs with formation of soft and hard segment are shown in Figure 2.3. The hard segments are formed by the reaction of diisocyanate with low molecular weight glycol, or diamine (chain extender). On the other hand, soft segments are formed by polyol (oligomer). The microphase separation of these two dissimilar segments produces regions of hard segment concentration (domains) which act as cross-link points for the soft segment. The network structure can be easily deformed above glass transition temperature (T_g) to give a temporary shape, the original shape can recover when the material heat above the glass transition temperature (Mondal et al., 2002).

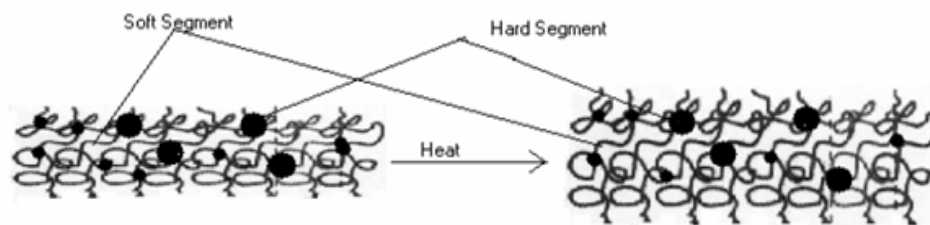


Figure 2. 3: Deformation of shape memory polyurethane (Leng et al., 2011)

Besides that, the soft segments, which are long-chain diols, are amorphous or have low crystallization and melting temperatures. They provide the final polyurethane with flexibility and control its low temperature properties. On the other hand, the hard segments are formed when bifunctional diisocyanate (OCN-R-NCO) and monomer diols (HO-R'-OH) react. The hydrogen bonds among urethane groups in hard segments (Figure 2.4) lead to crystalline or glassy phase, which is not soluble in the soft segments and this force causes of phase separation. The hard segment domains offer stiffness of the resultant materials. Therefore, the flexibility, strength and toughness of thermoplastic polyurethanes are dependent on the degree of phase separation of hard segments and soft segments domains, which is related to the structure of the poly diol, the choice of chain extender, the ratio of monomers, and the reaction process and conditions (Cao, 2008).

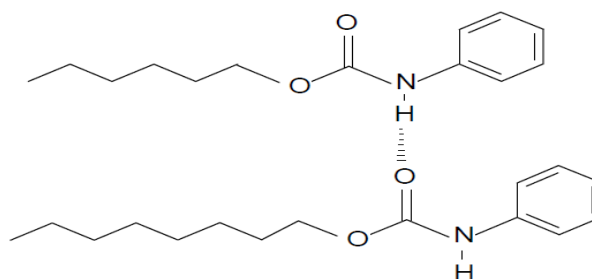


Figure 2.4: Interactions involving urethane groups

On the other hand, shape memory polyurethanes (SMPUs) remain one of the main classes of SMPs studied. Their attractiveness mainly lies in their ease of processing and low cost. Therefore, Ratna & Karger-Kocsis (2008) recently reviewed current advances in terms of the chemical structure/composition and shape memory property of SMPUs. These researchers found that optimized shape memory effects were obtained at a hard-segment content for glassy thermoplastic SMPUs and at a soft-segment for semicrystalline SMPUs (Mather et al., 2009).

Besides that, Park et al. (2014) studied regarding the shape memory behavior of crystalline shape memory polyurethane (SMPU) reinforced with graphene, which utilizes melting temperature as a shape recovery temperature in order to investigate the properties of SMPU. There are also researchers studied regarding the thermal, mechanical properties and shape memory effect by utilizing amorphous soft segment domain as reversible phase and crystalline hard segment domain as frozen phase in shape memory polyurethane (Jeong et al., 2000).

Nowadays, SMPU may be produced using natural oil polyol in order to improve the properties of SMPU as well as to reduce the cost usage of polyol from petroleum polyol. Therefore, many researchers conducted studies regarding SMPU from natural oil as it has become a great interest among researchers. Subtopic 2.4 will discuss in details regarding the utilization of natural oil in shape memory polyurethane.

2.3.1 Chemistry of Shape Memory Polyurethane

The polyurethane thermoplastic elastomer has three main basic materials which are polyol, diisocyanate and also chain extender. The selection of basic materials will determine the properties of the polyurethane.

2.3.1.1 Polyol

Polyol that has a flexible long chain will form a soft segment and acts as a backbone in the structure of polyurethane elastomer. There are two main groups of polyol that is mainly used in production of polyurethane which is polyether polyol and polyester polyol. Polypropylene glycol (PPG) and polytetramethylene glycol (PTMG) is an example of a polyether polyol which is normally used to produce polyurethane elastomer. PPG and PTMG produced by the addition polymerization of epoxy monomer. Polyethylene glycol (PEG) is also one of the examples of polyether polyol. Polyether polyols have a high hydrolysis stability as compared to polyester polyols and more easily designed when the polarity of the backbone is an important aspect of concern (Thomson, 2005).

Meanwhile, among the type of polyester polyol that is commonly used among researchers is polycaprolactone diol (PCL). Polyester polyol have oil resistance and better thermal properties than polyether making it an attractive choice as a soft segment of polyurethane. It also has a crystalline structure caused by the existence of a secondary power stronger than between force which is stronger within polyester chain as compared to polyether (Ionescu, 2005) that makes the resulting polyurethane stronger and sturdier. Besides that, vegetable oil polyols such as castor oil, soybean oil,

palm oil, and sunflower oil are also a type of polyester polyol. The focus of this study involves polyol produced from palm oil, which is the second most important vegetable oil after soybean oil.

On the other hand, vegetable oil molecules must be chemically transformed in order to introduce hydroxyl groups. Nevertheless, many reactions for preparing polyols from vegetable oils are not very selective. By-products, in addition to alcohol groups, are created during the transformation. Palm oil polyols (POP) is generally produced by converting palm oil to epoxidized palm oil (EPO) through the process of epoxidation followed by a reaction between the EPO and the polyhydric alcohol to form a polyol. This process involves the additional of an OH functional group of the C chain fatty acids in palm oil (Sambanthamurthi et al., 2000).

2.3.1.2 Diisocyanate

Diisocyanate is act as a hard segment in the polyurethane polymer when reacted with a polyol. This hard segment has a low molecular weight and capable of forming an interaction between the network via hydrogen bonds and form a hard segment domain. Isocyanates are chemical compounds from the isocyanic acid having NCO groups in its structure that will be react with OH group from polyol. There are two types of diisocyanate which is aliphatic diisocyanate and aromatic diisocyanate. In general, aromatic isocyanates are more reactive than aliphatic ones (Gabriel et al. 2014). Besides that, aromatic amines are commercially available and at a low-cost, due to these factors, 95% of commercial diisocyanates are based on toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). Meanwhile, aliphatic amines do not

exhibit favorable costs and are difficult to be commercialized as 1,6-hexamethylene diisocyanate (HDI) and 1,4-butane diisocyanate (BDI).

2.3.1.3 Chain Extender

Chain extenders are reactive low molecular weight compounds such as hydroxyl amines, diamines, and glycols. It is used to influence the end properties of polyurethanes during their synthesis. The chain extenders is reacted in the final stage with the isocyanate, polyol and affects considerably the polyurethane mechanical response as a result of the hard/soft segments interaction (Prisacariu and Scortanu, 2011). It is also divided into triol and linear polyols which is used with different molecular weight as chain extenders. Triol is usually used for chemical crosslinking while the linear polyol is used as a plasticizer for reducing pressure on final polymer (Clemitson and Clemitson, 2008). The most popular diols that are used among researchers are 1, 4-butanediol (BD), ethylene glycol and propylene glycol.

2.3.2 Structure of Shape Memory Polyurethane

In the shape memory polyurethanes, the hard segment and soft segment domains act as fixed and reversible phases, respectively. The SMPU has a mechanism that can be forms into two types which is chemical crosslinking and physical crosslinking of chain bonding. Chemical crosslink between polymer chains is based on the thermosetting SMPU which requires to hold the permanent shape. However, the chemical crosslink also will be prevent the polymer bonding to return to its original shape because of the bonding formed is in covalent bond (Behl and Lendlein, 2007).

Meanwhile, the physical crosslink is formed from the thermoplastic SMPU (D'hollander et al., 2009). The hard segment domain contains long of hydrogen bonding due to higher urethane formation and the bonding is serve as the physical crosslinks. On the other hand, the soft segments can be deformed by an external force at temperature above T_{trans} , the glass transition or melting temperature, and the temporary shape can be fixed by cooling the sample below T_{trans} . Shape recovery occurs as the specimen is heated again at or above T_{trans} . In this section, the shape memory polyurethanes are discussed based on two categories which is thermoset and thermoplastic shape memory polyurethanes.

2.3.2.1 Thermoset Shape Memory Polyurethane

The thermosetting shape memory polyurethanes have higher modulus as compared to thermoplastic shape memory polyurethanes. However, the thermosetting materials are difficult to process and are not reshapable. When undergoes reheating process, the chemical crosslinking that exist in SMPU preventing the polyurethane from remelt and reshape again. Therefore, very limited research activities in thermosetting shape memory polyurethane were found.

In the study of Lee et al., they were synthesized shape memory polyurethanes having crosslinks in either hard segments or soft segments with T_g as the transition temperature. The crosslinking at hard segment increasing the value of T_g compared to crosslinking in soft segment. Their mechanical result testing shows that the lower modulus of hard segment is at room temperature because of lower value of T_g will reduce its ability to withstand the load given. Besides that, the shape memory behavior of SMPU shows that the shape fixity for crosslinking in hard segment is lower than in