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**EFFECT OF DIFFERENT TYPE OF ISOCYANATES ON THE PROPERTIES
OF SHAPE MEMORY POLYURETHANE ELASTOMER BASED ON PALM
KERNEL OIL POLYOL**

By

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Dissertation submitted in fulfillment

of the requirements for the degree of Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

JUNE 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Effect of Different Type of Isocyanates on the Properties of Shape Memory Polyurethane Elastomer Based on Palm Kernel 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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ACKNOWLEDGEMENTS

This research was supported by Dr. Syazana Ahmad Zubir, the supervisor of the project. I wish to express my sincere thanks to Dr. Syazana Ahmad Zubir for her continuous supervision, assistance and support from the initial to the final stage of my final project. This dissertation would not be possible without her patient guidance, enthusiastic encouragement and constructive suggestions throughout the whole period. The valuable lessons learnt not only helped me in enhancing my knowledge, but the interpersonal skill and the positive attitude as well.

Besides, I would like to take this opportunity to express my gratitude to all the lecturers involved in my final year project for their precious guidance and opinions which are extremely valuable for my study both theoretically and practically.

Next, I wish to express my sincere thanks to all the technicians for the given technical support for this research throughout this period. They are keen in teaching and assisting me when dealing with the machines and equipment during my laboratory work. Their careful and precious guidance were extremely valuable for my study both theoretically and practically.

I also thank my parents and family members as well as my fellow coursemates for their constant encouragement, support and attention. Last but not least, I would like to express my gratitude to the postgraduate students who had provided insights and expertise that has greatly assisted the research.

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LIST OF ABBREVIATIONS

BD	1, 4-butanediol
Cd-Au	Cadmium-gold
COPUs	Castor oils based polyurethanes
Cu-Sn	Copper-tin
Cu-Zn	Copper-zinc
DBTDL	Dibutyltin dilaurate
DSC	Differential Scanning Calorimetric
DTG	Derivative Thermo-Gravimetric
FTIR	Fourier Transform Infrared Spectroscopy
HDI	1,6-Hexamethylene Diisocyanate
HMDI	4,4 Methylene-bis(cyclohexyl isocyanate)
IPDI	Isophorone diisocyanate
MDI	4,4'-Methylene diphenyl diisocyanate
-NCO	Isocyanate group
Ni-Ti	Nickel-titanium
Nitinol	Ni-Ti Naval Ordnance Laboratory
-OH	Hydroxyl group
PCL	Poly (caprolactone) diol
PE	Polyethylene
PEG	Poly (ethylene) glycol
PKO	Palm Kernel Oil
PLA	Poly lactic acid
PPG	Poly (propylene) glycol

PTFE	Poly (tetrafluoroethylene)
PTMG	Poly (tetramethylene) glycol
PVC	Poly (vinyl chloride)
SMA _s	Shape memory alloys
SME	Shape memory effect
SMM _s	Shape memory materials
SMP _s	Shape memory polymers
SMPU	Shape memory polyurethane
SOPU _s	Soybean oil based polyurethanes
TGA	Thermal Gravimetric Analysis
TDI	Toluene diisocyanate
UTM	Universal Testing Machine
XRD	X-ray Diffraction

LIST OF SYMBOLS

cm	Centimetre
mm	Millimetre
mg	Milligram
G	Gram
min	Minute
rpm	Revolutions per minute
°C	Degree Celsius
%	Percentage
% χ_c	Percent crystallinity
ΔH°_m	Heat of fusion
ΔH_m	Enthalpy change
N_{OH}	Hydroxyl number
T_{trans}	Transition temperature
T_g	Glass transition temperature
T_m	Melting temperature
Θ	Angle
θ_{cr}	Constraint removal angle
θ_f	Final angle
Λ	Wavelength
kN	Kilo Newton
Å	Ångström

**KESAN ISOSIANAT YANG BERBEZA TERHADAP SIFAT ELASTOMER
POLIURETANA MEMORI BENTUK BERASASKAN POLIOL MINYAK
ISIRONG SAWIT**

ABSTRAK

Prestasi elastomer poliuretana memori bentuk (SMPU) bergantung kepada komposisi kimia, struktur kimia, tahap ikatan hidrogen serta struktur pemisahan fasa mikro. Kertas kerja ini melaporkan kajian berkenaan SMPU berasaskan polioliol minyak isirong sawit (PKO). Dalam kajian ini, nisbah molar dan jenis isosianat telah digunakan sebagai pemboleh ubah yang dimanipulasi. SMPU dihasilkan melalui dua langkah pempolimeran pukal dengan menggunakan polikaprolakton diol dan polioliol minyak isirong sawit (PKO) sebagai segmen lembut, 1,6-heksametilena diisosianat/ 4,4 metilena-bis (sikloheksil isosianat)/ isoforon diisosianat dan 1,4-butana diol sebagai segmen keras dengan dibutiltin dilaurat sebagai pemangkin. Beberapa pencirian seperti Spektroskopi Infra-Merah, Kalorimetrik Pengimbas Pembezaan, Analisis Termal Gravimetrik, Pembelauan sinar-X dan ujian tegangan telah dijalankan untuk menyiasat sifat-sifat struktur, termal dan mekanikal SMPU. Ujian memori bentuk dijalankan untuk menyiasat sifat memori bentuk SMPU. Didapati bahawa penghabluran segmen lembut SMPU dan ketetapan bentuk SMPUs berkurangan dengan penambahan kandungan segmen keras. Secara keseluruhannya, sampel IPDI 154 menunjukkan nilai modulus dan sifat ketetapan bentuk yang lebih tinggi berbanding dengan sampel HDI 154 and HMDI 143 manakala sampel HMDI+IPDI 165 menunjukkan sifat ketetapan bentuk

yang lebih baik, nilai modulus dan kekuatan tegangan yang lebih tinggi berbanding sampel IPDI 165.

**EFFECT OF DIFFERENT ISOCYANATES ON THE PROPERTIES OF SHAPE
MEMORY POLYURETHANE ELASTOMER BASED ON PALM KERNEL OIL
POLYOL**

ABSTRACT

The performance of the shape memory polyurethane (SMPU) elastomers depends on chemical composition, chemical structure, the extent of hydrogen bonding and microphase-separated structure. This paper reports the study of palm kernel oil (PKO) polyol based SMPU. In this study, the molar ratio and types of isocyanate were used as manipulated variables. The SMPUs were synthesized via a two-step bulk polymerization method using polycaprolactone diol and PKO as soft segment, 1,6-hexamethylene diisocyanate/ 4,4 methylene-bis(cyclohexyl isocyanate)/ isophorone diisocyanate and 1,4-butanediol as the hard segment with dibutyltin dilaurate as the catalyst. Several characterizations such as Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetric, Thermal Gravimetric Analysis, X-ray Diffraction and tensile test were carried out to investigate the structural, thermal and mechanical properties of SMPUs. Shape memory test is performed to investigate the shape memory behaviour of SMPUs. It was found that the crystallinity of SMPU soft segments and shape fixity of SMPUs decreases with increasing of the hard segment content. In overall, IPDI 154 sample demonstrate higher modulus value and shape fixity properties as compared to HDI 154 and HMDI 143 samples while HMDI+IPDI 165 sample shows better shape fixity, higher modulus value and tensile strength as compared to IPDI 165 sample.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polyurethane is a polymer which composed of a chain of organic units joined by carbamate (urethane) links. Most of the polyurethanes are thermosetting polymers which cannot be melted and remoulded when heat is applied however thermoplastic polyurethanes do exist too. Generally, polyurethane elastomer is synthesized using three major components: polyols, isocyanates and chain extenders. Other agents such as catalysts and stabilisers are sometimes added to support the chemical process. Figure 1.1 shows the reaction between polyol, diisocyanate to form polyurethane. Besides that, the properties of polyurethane are dependent on the types of isocyanate and polyol. High amount of the cross-linking within hard segments will produce a tough and rigid polymer while mobile and flexible chains from soft segment will produce elastic polymer.

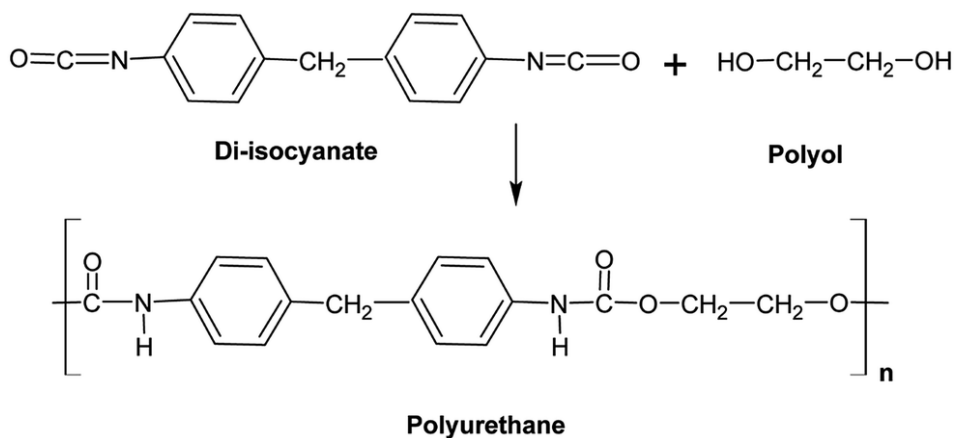


Figure 1.1: Reaction between diisocyanate and polyol to form polyurethane (Akindoyo *et al.*, 2016)

Nowadays, polyurethane is a leading member of the wide-ranging and highly diverse family of polymers. It is versatile polymeric material, which are extensively used in biomedical applications due to their diversity in the structure and properties. They are investigated to use in long term implants such as vascular grafts, cardiac pacemakers as well as tissues replacements due to its biocompatibility, outstanding mechanical flexibility and processability. Besides that, due to its properties including lightweight, excellent strength, low thermal conductivity and high weight-carrying capacity, polyurethane is commonly used such as adhesives and coating materials, synthetic leathers, building construction materials, surgical drapes, wound dressings and automotive (Cooper and Guan, 2016).

Shape memory polyurethane (SMPU) is a smart polymeric material, which has the ability to change from a temporary shape to a memorized permanent shape when exposed to an external stimulus. The external stimuli can be in the form of heat, light, electricity, magnetic field, change in pH and even moisture (Yahia, 2015). SMPUs have the ability to present different mechanical behaviour due to the existence of phase separated structure which is known as soft and hard segment domains. The hard segments such as isocyanates and chain extenders play a role for permanent shape by physical cross-links with high melting temperature hydrogen bonding and crystallization. On the other hand, polyols as soft segments provide reversible phase transformation which is important to achieve shape memory effect (Jung and Cho, 2010).

SMPU has a unique structural characteristic because of the presence of inherent incompatibility between soft and hard segments (Thakur and Hu, 2017). Urethane hard segments have higher polarity as compared to the soft segment and thus, it will result in the formation of two-phase microstructure. Generally, the shape of thermally responsive

shape memory polymers can be readily changed above the shape memory transition temperature (T_{trans}). The T_{trans} can be either a glass transition temperature (T_g) or a melting point (T_m). If SMPU is stretched above its T_{trans} for a long period of time, large scale movement of polymer chains are favourable since the chains are flexible. The freezing of the molecular motion of the polymers below T_{trans} will prevent the molecular chains from reforming the coil-like structures. Hence, temporary, programmed shape is fixed. Once being heated over T_{trans} again, the oriented polymer chains are softened and formed a more stable coiled conformation. Hence, the original shape of the polymer can be recovered automatically.

At present, petroleum has been the feedstock for most polyols and isocyanates for the production of polyurethane. However, due to increase annual consumption of polyurethane, the rate of depletion of these materials has caused escalating in price of petroleum (Zhang and Kessler, 2015). Moreover, the need for high technology processing system has caused researchers to look for utilizing plant that can serve as alternative feedstock for monomer in polymer industry. The environmental concerns also have prompt interest in development of bio-renewable feedstock such as vegetables oil to replace petroleum-based polyols in the production of some polymeric materials. As a result, synthesizing polyurethane using bio-based polyols from various vegetable oils such as palm oil, soybean oil, rapeseed oil, castor oil and other materials such as molasses, starch, potato, and wheat (Septevania *et al.*, 2015) became great interest among the researchers in order to replace the existing petrochemical-based polyols.

Generally, the structure of natural oils depends on the composition, type and distribution of fatty acids in the triglyceride molecule. Applicability of oil is determined according to their composition and price. Most of the natural oils do not have hydroxyl groups which are responsible to form urethane links with isocyanate except few oils

such as castor oil and lesquerella oil. Various polyols can be obtained by epoxidation of vegetable oils followed by oxirane ring opening in order to convert epoxy groups into hydroxyl groups. According to Zhang colleagues (2015), different types of ring opening chemical agent will create polyols with different functionalities for polyurethanes. Hydrogen gas (H_2), organic acids, hydrohalic acids and amines are examples of ring opening chemical agents, which are used to initiate the ring opening reaction.

Besides that, the properties of polyurethanes strongly depend on the types of polyol used. In a study conducted by Kalita and Karak (2014), different types of vegetable oils polyols were mixed with toluene diisocyanate (TDI) to fabricate bio-based SMPUs. The results showed that castor oil based polyurethane exhibited the highest tensile strength and shape recovery as compared to mesua ferrea and sunflower oils based polyurethanes. This is because of the presence of more physical cross-linking due to high urethane linkages. Urethane linkages can store the deformed energy in the system and immediately release the deformed energy once undergo reheating process. Hence, cross-linking is very critical to the shape recovery effect. Besides that, all the bio-based polyurethane samples showed higher shape fixity than the oil free polyurethane due to the presence of long chain fatty acid moieties which will enhance the secondary interactions during vitrification process.

1.2 Problem Statement

Previous works on SMPs have focused on the developmental progress in achieving, tailoring and utilizing the shape memory effect. The main types of polymer used in medical field are polyolefins, poly (tetrafluoroethylene) (PTFE), poly (vinyl chloride) (PVC), methacrylates, polyesters, polyethers and polyamides (Maitz, 2015).

However, according to the research work on the shape memory effect of polylactic acid (PLA)-based craniofacial plates, PLA materials do not possess good shape recovery properties without addition of additional physical or chemical cross-linking. As a result, moderate shape recoveries observed in the plating studies (Yakacki and Gall, 2010). Besides that, main applications of polyolefins polyethylene (PE) are used as sliding surfaces of artificial joints. Yet, PE can undergo oxidation especially gamma sterilization, which increases hydrophilicity, recrystallization and makes the polymer more brittle (Maitz, 2015). Thus, polyurethane has been developed to be used in medical applications due to limitation of those polymers.

Most polyols used in polyurethane industry are petroleum-based where coal and crude oil are used as starting raw materials. High rate of depletion and escalating in price of the materials as well as high technology processing system have prompt interest in utilizing plants that can serve as alternative feedstock of monomers for the polymer industry. As an example, palm kernel oil based feedstocks able to show less total environment impact due to significant reduction in fossil fuel depletion and can enhance the properties of SMP. Therefore, the aim of the study is to reduce the usage of petrochemical-based polyol in SMPU by substituting with palm kernel oil during synthesis.

The properties of SMPU can be affected by its main composition, such as type of polyol, isocyanate and chain extender. In general, polyester polyol possessed stronger bond acceptor as compared to polyether polyol. As a result, polyester polyol based SMPU tends to have better crystalline structure than polyether polyol based SMPU. However, in this study, different types of isocyanate for polyurethane synthesis are introduced in order to produce SMPU with best properties. This is because a unique structure of SMPU is determined by the structure of the starting material used while the

structure of the isocyanates has a profound impact on the thermal and mechanical properties of SMPUs. As an example, high symmetry and rigidity in the p-phenylene diisocyanates will result in high modulus and excellent tensile strength. On the other hand, bulkiness and methyl groups on the phenyl ring of the diisocyanates will also affect the mechanical properties and crystallizability of the SMPUs (Rehman, 2010).

Generally, the synthesis of SMPUs can be achieved by employing solution polymerization and bulk polymerization techniques. The presence of solvent can assist transfer of heat produced during solution polymerization process and dilution effect makes it easier for stirring of the polymerization solution (Hoogenboom *et al.*, 2016). However, the major drawbacks of the process are the necessary of removal of the solvent and difficult to obtain product with free contaminants other than by products or side reactions. On the other hand, bulk polymerization has become the main industrial process for polyurethane production due to its environmental friendly polymerization method as no purification required. Moreover, this method is relatively simple and able to obtain product with high purity.

On the other hand, two-step bulk polymerization process provides a more typical soft-hard-soft block sequence because the chemistry of the reaction is easier to be controlled (Hosseini and Makhoulf, 2016). This structural regularity may impart better mechanical properties to the polyurethane since the hard segments more easily crystallize to form physical cross-link point. It also allows partial dissipation of the exotherm before the formation of polyurethane. Hence, two-step polymerization is more favourable for synthesis of SMPU.

1.3 Research Objectives

The research objectives of this study are:

- i. To synthesize SMPU elastomer based on palm kernel oil polyol via two-step bulk polymerization method.
- ii. To examine the effect of different types of isocyanate on the properties of the shape memory polyurethane elastomer based on palm kernel oil polyol.
- iii. To characterize the tensile and shape memory properties of the polyurethane elastomer based on palm kernel oil polyol.

1.4 Scope of Research

The purpose of this study is to synthesize palm kernel oil (PKO) polyol based SMPU via two-step bulk polymerization process. The ratio of PKO to PCL used in SMPU production is fixed at 0.2 and 0.8 respectively.

Furthermore, different molar ratio and three types of isocyanate are varied in order to study its effect towards the final properties of SMPU. The isocyanates used to synthesis SMPU are 4,4-methylene-bis(cyclohexyl isocyanate) (HMDI) / 1,6-hexamethylene diisocyanate (HDI) / isophorone diisocyanate (IPDI). The SMPU samples produced will then undergo various characterizations in order to investigate their respective properties. Shape memory testing is done to determine the shape memory effect of SMPUs. The shape memory behaviour is determined by measuring the percentage of shape fixity and shape recovery of the samples. Tensile testing is also performed on SMPUs by using Instron Universal Testing machine. In addition, the crystalline phase of polyol soft segment is characterized by X-Ray Diffraction (XRD) and Differential Scanning Calorimetric (DSC). Fourier Transform Infrared

Spectroscopy (FTIR) is used to analyse elemental bonding and information on chemical structure that presents in SMPUs. The thermal property of SMPUs is determined by using Thermal Gravimetric Analysis (TGA) and DSC.

CHAPTER 2

LITERATURE REVIEW

2.1 Shape Memory Materials

Shape memory materials (SMMs) are stimuli-responsive materials. These materials are featured by the ability to regain the trained shape from a deformed shape when external stimuli such as pH, heat or electricity is applied. When the material is recovered to its original reference state by a change in temperature, it is known as thermally induced shape memory effect. Figure 2.1 shows the schematic process of programming and recovery of a SMM.

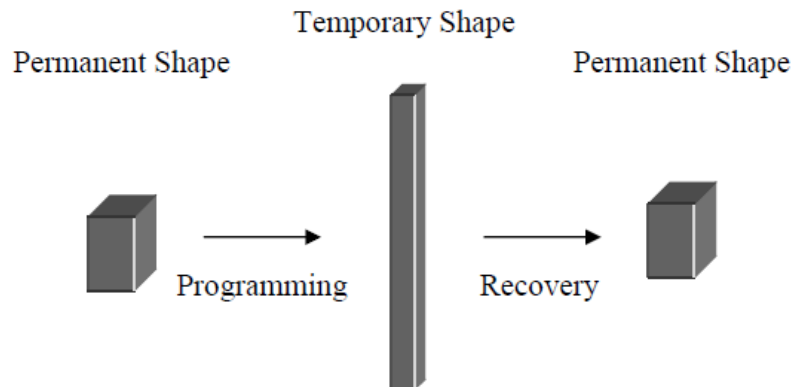


Figure 2.1: Schematic representation of shape memory effect (Lendlein and Kelch, 2002)

SMMs have received increasing attention from researchers and scientists due to their novel performance such as high damping capacity, adaptive responses, shape memory and superelasticity capability which are contributed by the phase transitions in the materials (Wei *et al.*, 1998). Generally, SMMs can be divided into shape memory

polymers, shape memory alloys, shape memory ceramics, shape memory gels and shape memory hybrids. The shape memory effect in SMMs can be utilized in many fields for instance aerospace engineering (e.g., antenna for satellites or self-deploying sun-sails) and medical devices (e.g., stents, filters and sutures).

2.1.1 Shape Memory Alloys

Shape memory alloy (SMA) or “smart alloy” in solid state was first discovered by Arne Oleander in the year 1932. Later, Oleander found that solid cadmium-gold (Cd-Au) alloy had the capabilities to revert to its original configurations when heated after plastically deformed. In 1938, characteristics of shape memory effect in copper-zinc (Cu-Zn) and copper-tin (Cu-Sn) were discovered by Greninger and Mooradian (Krishnan *et al.*, 2017). A decade later, the fundamental phenomenon of the memory effect governed by the thermoelastic behaviour of the martensite phase was discovered by Chang and Read. SMAs started to gain attention in the early 1960s after William Buehler and Frederick Wang revealed nickel-titanium (Ni-Ti) alloy or nitinol (Ni-Ti Naval Ordnance Laboratory) possessed shape memory effect (Mohd Jani *et al.*, 2014).

SMAs belong to a class of SMMs. It has the ability to memorise and recover into their previous shape when subjected to certain stimulus such as thermomechanical or magnetic variations. SMAs characteristic is characterized by the shape memory effect and by the superelasticity. Superelasticity in alloy is associated with the recovery from loading-originated strains of up to 8% or 10% without significant residual strains. On the other hand, shape memory effect of alloy is characterized by the capacity of recovering residual strains developed after cyclic loading with a temperature variation (Lobo *et al.*, 2015).

SMAAs can exist in two state phases with three different crystal structures, which are austenite, twinned martensite and de-twinned martensite (Mohd Jani *et al.*, 2014). Austenite is known as parent phase while martensite is known as softer product phase. Transformation from the parent phase into product phase can be prompted by temperature reduction or increase of stress. The martensite structure has a lower symmetry compared to austenite. Figure 2.2 shows schematic representation of the shape memory effect and superelasticity of shape memory alloy. Generally, SMAAs are characterized by four transition temperatures, which are austenite start temperature (A_s), austenite finish temperature (A_f), martensite start temperature (M_s) and martensite finish temperature (M_f) (Lobo *et al.*, 2015). When the temperature, T , is below transition temperature M_f , the stable phase is martensite. In the meantime, the microstructure is known as “self-accommodating twins”. This is due to the martensite structure is soft and can be easily deformed by de-twinning. On the other hand, when the temperature, T , is higher than A_f , austenite is stable. SMAAs will recover to the original shape and converted to high strength austenite condition upon heating above the transition temperature, A_f . Both martensite and austenite phases are stable for temperature values between A_s and M_s .

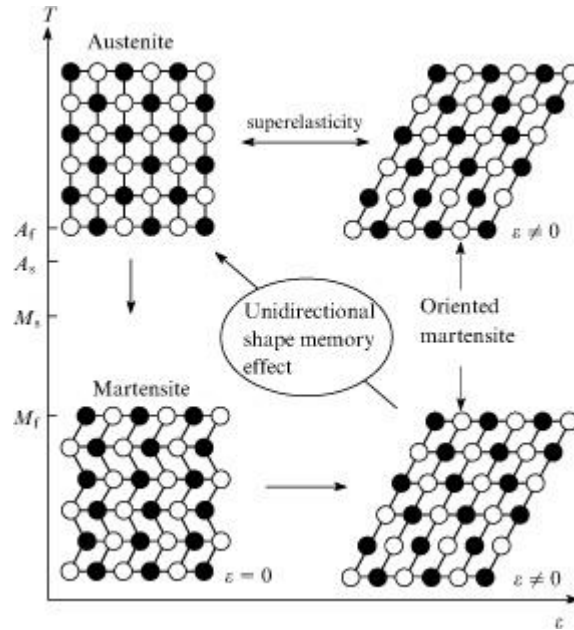


Figure 2.2: Schematic representation of the SME and superelasticity in SMA

(Pogrebnjak *et al.*, 2013)

Among the various alloy systems which exhibit shape memory effect, copper-based SMAs such as copper-zinc-aluminium (Cu-Zn-Al) and copper-aluminium-nickel (Cu-Al-Ni) as well as nickel-titanium (Ni-Ti) SMAs have drawn great interest among the researchers to study extensively over the years. Generally, copper-based SMAs are easier to process and fabricate when compared to Ni-Ti SMAs. Besides that, copper-based SMAs can be made from relatively inexpensive metals by conventional metallurgical processes which makes them the cheapest of the commercial SMAs. However, these alloys are more brittle than Ni-Ti when in the polycrystalline state. Consequently, they cannot be worked easily high degree of order and high elastic anisotropy of the parent phase, which is austenite (Sathish *et al.*, 2014).

Ni-Ti alloy system has the ability to regain to its original shape even after large amount of deformations and maintain constant applied force in correspondence of

significant displacements. Ni-Ti alloys are generally more expensive when compared to copper-based SMAs as all melting and joining processes such as brazing, welding or soldering must be done in vacuum or in an inert atmosphere due to the high reactivity of titanium. In spite of high manufacturing cost in producing Ni-Ti, their good workability in the martensite phase, biocompatibility and good resistance to fatigue and corrosion enable them to be used in a wide variety of applications such as biomedical device, biomedical implant, actuators, and sensor (Petrini and Migliavacca, 2011). According to Gravina *et al.* (2014), Ni-Ti alloys inherent unique properties such as high resilience, high elastic limit and low module of elasticity and rigidity. As a result, Ni-Ti alloys have been commercialized in orthodontic purposes.

SMAs are supreme but they also do have some drawbacks such as high manufacturing cost, limited recovery and complicated surgical problems. Thereby, new SMMs with similar shape memory effect such as shape memory polymers have been synthesized.

2.1.2 Shape Memory Polymers

Shape memory polymers (SMPs) are an emerging class of active polymers which have dual-shape capability. They have the ability to return from a temporary deformed state to their permanent original shape upon application of an external stimulus such as heat, light, electricity, magnetic field, change in pH and even moisture (Yahia, 2015).

The SMPs are of great interest for fundamental research and technological innovation since the middle of the 1980s due to a multitude of desirable qualities such as high recovery strain within a wide range of stimuli, biocompatibility and

biodegradability with an opportunity to adjust the degradation rate, easy processability, low density as well as potentially recyclable at relatively low cost (Pilate *et al.*, 2016). Thus, applications of SMPs are spanning various areas of everyday life. For example, potential applications of the SMPs are medical and biomimetic devices, self-deployable sun sails in spacecraft, self-disassembly mobile phones, actuators, sensors, smart fabrics and heat shrinkable tubes for electronics or films for packaging (Behl and Lendlein, 2007; Pilate *et al.*, 2016).

Generally, SMPs are equipped with suitable stimuli-sensitive switches. As shown in Figure 2.3, the polymer network consists of netpoint (hard segment) and molecular switch (soft segment) in order to achieve SME (Behl and Lendlein, 2007). The netpoint provides entropic elasticity and is responsible to regain permanent shape of the polymer during shape recovery process. The hard segments in the SMP can be created by physical or chemical cross-linking. The permanent shape of polymer can be obtained when the hard segment inhibits the plastic slip of the molecular chains by physical cross-linkage points among them. On the other hand, molecular switch is reversibly sensitive to certain external stimuli and is responsible to obtain temporary shape during shape fixity process. The T_{trans} of the switching domains is virtually acted as the T_{trans} for triggering the shape memory effect. The switching domains are flexible if the working temperature is above the T_{trans} but rigid if the working temperature is below the T_{trans} . As a result, SMPs can undergo large amount of deformations at temperature above the T_{trans} and then fix into a temporary shape at temperature below the T_{trans} due to frozen of the mobility molecular chains.

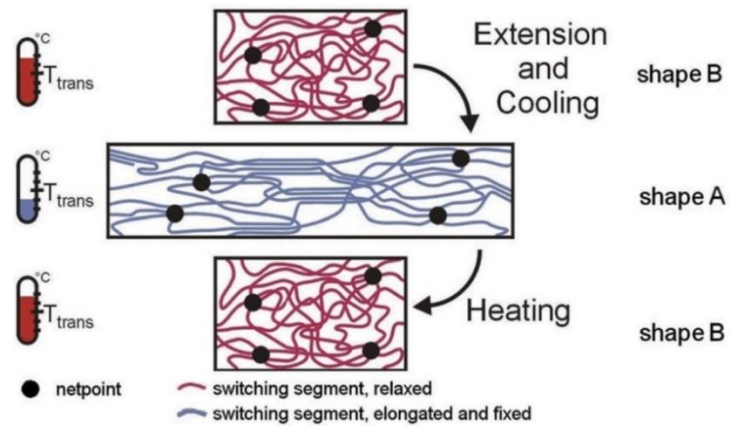


Figure 2.3: Molecular mechanism of SME of thermally induced SMP (Behl and Lendlein, 2007)

2.1.2.1 Shape Memory Effect

Shape memory polymers (SMPs) are smart materials which featured by the ability to regain original shape from temporary shape when a particular stimulus (heat, light, electricity, and entropy driven deformation) is applied (Ahmed *et al.*, 2015). This effect is known as the shape memory effect (SME). Figure 2.4 illustrates the example mechanism of a SMM.

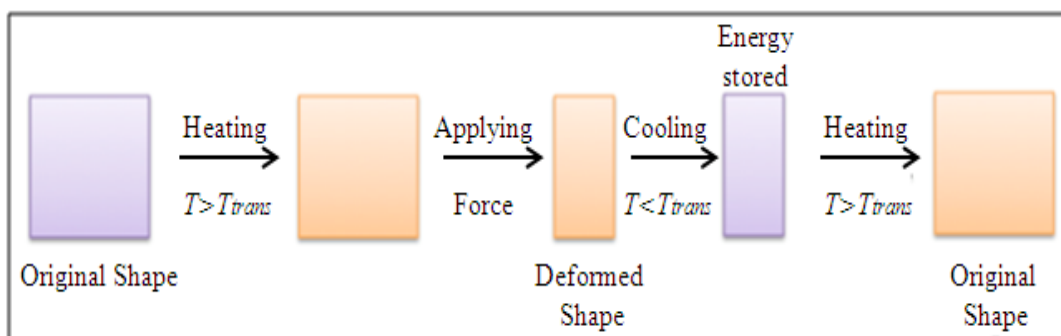


Figure 2.4: Mechanism of SME (Erkeçoğlu *et al.*, 2016)

There are two types of shape memory behaviour namely; one-way shape memory (OWSM) behaviour and two-way shape memory (TWSM) behaviour. In OWSM behaviour, the permanent shape of the sample is transferred to the temporary shape by the programming process. The programming process either consists of heating up the sample, deforming, and cooling the sample, or drawing the sample at a low temperature (cold drawing).

When material is heated above its T_{trans} , it will regain into original shape by releasing the deformation. However, no recovery of the temporary shape can be observed when temperature is reduced to below T_{trans} . This phenomenon is due to cooling caused to store the strain at below T_{trans} . On the other hand, material exhibits TWSM behaviour can undergo a change in shape when heating above T_{trans} and obtain another configuration with subsequent cooling (Ahmed *et al.*, 2015).

2.2 Shape Memory Polyurethane

Shape memory polyurethanes (SMPUs), also known as urethanes, are characterized by the urethane linkage: $-\text{NH}-\text{C}(=\text{O})-\text{O}-$. Generally, polyurethanes are formed by the reaction of molecules containing two or more isocyanate groups ($-\text{N}=\text{C}=\text{O}$) with polyol molecules containing two or more hydroxyl groups ($-\text{OH}$) as shown in Figure 2.5. Although the main chemical moiety is the urethane group, other groups, such as urea, ether, ester, amide, allophanate and biuret linkages may be formed depending on the condition and the types of catalysts used. During synthesis of polyurethane, small molecule chain extenders such as alcohol or amine can be chemically inserted between the urethane groups in order to increase the molecular weight of the end product. Besides that, this reaction is carried out in the presence of catalysts so that chain extension reactions rate can be enhanced.

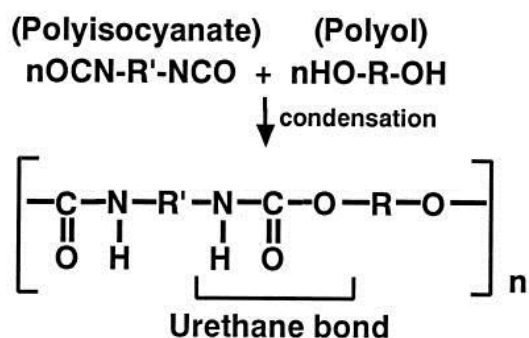


Figure 2.5: Structure of polyurethane (Akutsu *et al.*, 1998)

The structure of polyurethanes is considered as multi-block copolymers with an alternating sequence of hard and soft building blocks. The isocyanate and chain extender formed the hard segment while the soft segment is usually polyol of varying molecular weight. As shown in Figure 2.6, the hard crystalline segment acts as physical cross-links and as fillers within the amorphous soft segment matrix. The building blocks of polyurethanes phase separate on a microscopic scale occurs upon cooling process due to thermodynamic incompatibility between hard and soft segments. Due to easy segmental rotations of soft segment at ambient temperature, polyurethane is imparting with desired elastomeric properties (Mehl *et al.*, 2000).

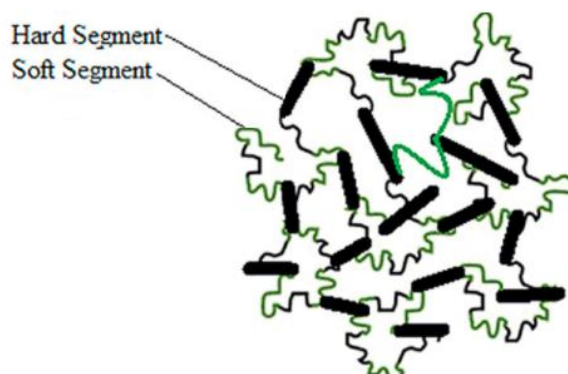


Figure 2.6: Morphological model of polyurethane (Shoaib *et al.*, 2017)

SMPU can be classified into two types and they are named according to the polyol used during synthesis: polyether SMPUs and polyester SMPUs. Generally, polyether polyol based SMPUs are more hydrolysis-resistant as compared to polyester polyol based SMPUs. As an example, SMPUs with poly (tetramethylene) glycol (PTMG) possessed outstanding microbial and hydrolysis resistance and excellent dynamic properties such as resilience and retention of elasticity at low temperature. On the other hand, polyester polyol based SMPUs are extensively used in foams, elastomers and coating applications due to their superior thermal and oxidative stability as well as excellent abrasion resistance. Previously, polyester SMPUs had attracted attention of the researchers because of its biodegradability properties. According to Nakajima-Kambe *et al.* (1999), polyester based SMPUs is vulnerable to microbial attack by microorganisms, especially fungi and bacteria. The microbial degradation is thought to be initiated by hydrolysis of the ester bonds by some hydrolytic enzyme, such as esterases.

Besides that, polyurethanes also can be classified into thermoset SMPUs and thermoplastic SMPUs based on the types of cross-links. Thermoset SMPUs are well known for their superior degree of shape recovery afforded by rubbery elasticity due to the nature of permanent cross-linking, tunable work capacity during recovery achieved by adjustable rubbery modulus through the extent of covalent cross-linking and an absence of molecular slippage between chains due to strong chemical cross-linking (Liu *et al.*, 2007). However, it is understood that thermoset SMPUs cannot be reprocessed, or, in the context of shape memory, the permanent shape of classical thermoset SMPUs cannot be altered. Hence, this reason has brought to the development of thermoplastic SMPUs.

On the other hand, thermoplastic polyurethanes are a linear segmented block copolymer consists of hard and soft domains that served as the physical cross-linkers. These cross-linkers act as permanent entanglement to prevent the slippage of the molecular chains. According to Lendlein and Kelch (2002), the hard segment phases with the highest T_{trans} act as physical net points in the polymer structure and responsible for the permanent shape. When the working temperature is above this transition temperature, the polymer starts to melt and can be processed. A second phase, also known as reversible switching segment acts as a molecular switch and responsible for fixation of the temporary shape. The temporary shape of the polymer can be fixed by cooling the polymer below the T_{trans} either glass transition (T_g) or melting temperature (T_m). Reheating the polymer above T_{trans} will cleaves the physical cross-links in the switching phase and thus induced the shape recovery.

2.2.1 Mechanism of Shape Memory Polyurethane

Shape memory can be triggered by light, heat, magnetic field, electric field, chemical and other external stimuli. The change in shape of the polymer caused by a change in temperature is known as thermally induced shape memory effect. SMPUs are composed of incompatible hard and soft segments which lead to present of microphase separated structure. The SME of segmented polyurethane is due to the network structure formed by hard and soft block. The hard segment blocks are formed by the reaction of isocyanates with chain extender. The hard segment blocks are responsible for imparting stiffness to the material. On the other hand, soft segments are formed by polyol and usually used to control the elastic behaviour of the polyurethanes.

Phase transition of SMPU accompanies a great change in its physical properties. As shown in Figure 2.7, the polymer achieves an elastic rubbery state at higher temperatures (above its T_g) and in a glassy state at lower temperatures. Due to the lower rubbery modulus at higher temperatures, polymers can be subjected to a very large amount of deformation. Besides that, the glassy modulus is generally at least two orders of magnitude stronger than the rubbery modulus (Wei *et al.*, 1998). Hence, the stored elastic stress is not large enough to drive the reverse deformation in the glassy state when the external load is removed. The deformed shape of the polymer can be fixed in the glassy state on quenching or after cooling under load to the lower temperatures. On the other hand, deformed shape of shape memory polymer can be recovered when the material is heated at higher temperature. Basically, ordinary polymers cannot fully restore their residual inelastic deformation upon reheating to the rubbery state. However, SMPs able to regain almost all the residual deformation after reheating process.

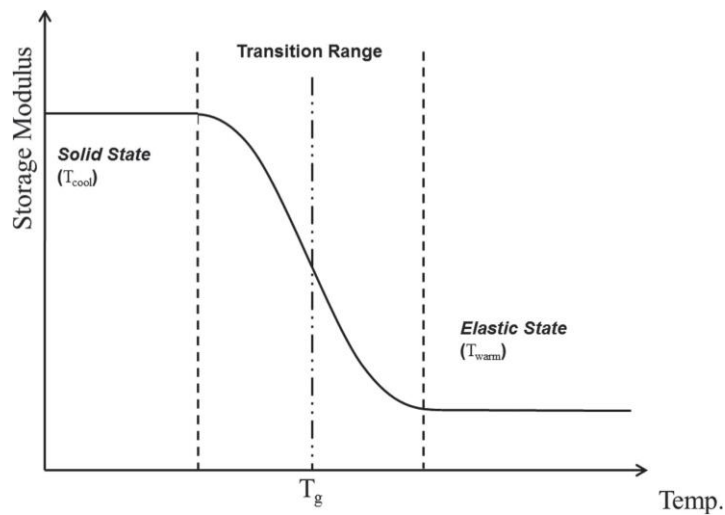


Figure 2.7: Temperature dependent properties of the SMPU (Patil and Song, 2017)

The features of a polymer required in order to induce good shape memory behaviour are a sharp transition from glassy state to rubbery state that can be used to promptly fix the secondary shape at low temperatures and trigger shape recovery at high temperatures. In addition, superelasticity (high deformability, low loss modulus) above the transition temperature which will leads the shape recovery and avoids residual strain (permanent deformation) as well as complete and rapid fixing of the temporary shape by immobilizing the polymeric chains without creep thereafter also necessary for superb shape memory behaviour (Liu *et al.*, 2007)

2.2.2 Polyurethane Building Blocks

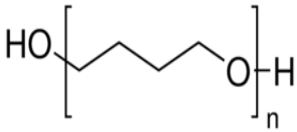
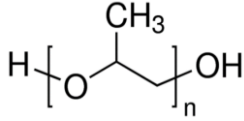
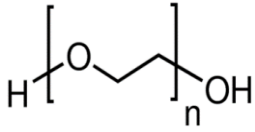
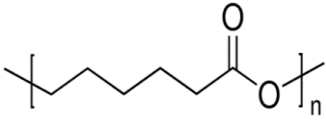
The starting materials to synthesis SMPUs are polyol, isocyanate and chain extender. The chemical and physical nature of these selected components will affect the final properties of produced SMPU.

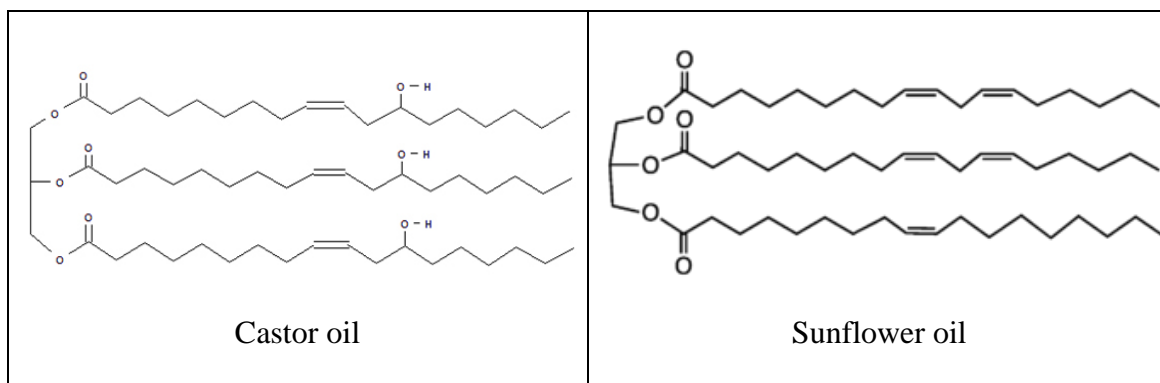
2.2.2.1 Polyols

Polyol is a relatively high molecular weight alcohol compounds which containing multiple hydroxyl (OH) groups. The reaction between the hydroxyl group and diisocyanate will produce polyurethane. Basically, the properties of the polyurethane are depend on the molecular weight and degree of cross-linking of the polyol. As an example, low molecular weight or highly branched polyol yield rigid polyurethane while high molecular weight or less branched polyol produce flexible polyurethane. Thus, the toughness and flexibility of polyurethane is mainly derived from polyol. Besides that, amorphous or crystalline state of SMPU reversible phase is also dominated by the nature of polyol.

There are two main groups of polyols, namely polyester polyol and polyether polyol. Polyester polyol is produced by polycondensation of di- or polycarboxylic acids with di- or polyalcohols. Poly (caprolactone) diol (PCL) is an instance of widely used polyester polyol due to its biodegradable properties. On the other hand, polyether polyol is produced by the alkali-catalyzed polymerization of ethylene oxide and propylene oxide with low molecular weight di- and polyfunctional alcohols or amines are used as initiators. The most used polyether polyols are poly (tetramethylene) glycol (PTMG), poly (ethylene) glycol (PEG) and poly (propylene) glycol (PPG). Other than that, vegetable oil such as castor oil, palm oil and sunflower oil are mostly used to synthesis vegetable oil based polyurethanes due to deficiency of petroleum products and stringent environmental rules and regulations. Table 2.1 illustrates chemical structures of common polyol compounds.

Table 2.1: Common used polyols for polyurethane synthesis (Sigma-Aldrich, 2018; Liu *et al.*, 2015)

 <p>Poly (tetramethylene) glycol (PTMG)</p>	 <p>Poly (propylene) glycol (PPG)</p>
 <p>Poly (ethylene) glycol (PEG)</p>	 <p>Poly (caprolactone) diol (PCL)</p>



Hydroxyl number of polyols is of the important parameter which could affect the shape memory effect of the SMPUs greatly. This is because hydroxyl groups in polyols are responsible for the reaction with isocyanate to form urethane bonds. Ahmad *et al.* (2012) found that polyols with a higher functionality are more reactive and can produce more cross-links. Hence the polyurethane will possess better mechanical properties. Nowadays, most of the SMPUs are synthesized using polyols with low molecular weight ranging from a few hundreds to a few thousand (200~3,000) g/mol and high functionality ($N_{OH} > 50$). The polyols with lower molecular weight and higher functionality ($N_{OH} > 50$) will have greater number of cross-link points and stronger bonding due to the short molecular chains, thus higher intermolecular interactions at soft segments. On the other hand, polyols with high molecular weights possess lower intermolecular interactions at soft segments due to the limited number of cross-link points.

2.2.2.2 Isocyanates

Isocyanates are unique and essential monomers required for polyurethane synthesis. Isocyanates are highly reactive chemicals which containing the functional group $-N=C=O$. Isocyanates can be categorised based on the number of $N=C=O$ groups

present in the molecule: monoisocyanates (one NCO group), diisocyanate monomers (two NCO groups) or polyisocyanates (multiple NCO groups). Generally, diisocyanate monomers are more significant as the two NCO groups allow direct polymerization reaction with polyols to form polyurethanes.

Besides that, isocyanate compounds can be either aromatic or aliphatic in nature. Currently, the most frequent used aromatic isocyanates in polyurethane industry are 2,4-toluene diisocyanate (2,4-TDI), 2,6-toluene diisocyanate (2,6-TDI) and 4,4'-methylene diphenyl diisocyanate (MDI), whereas HDI, IPDI and HMDI are the examples of aliphatic diisocyanates. Table 2.2 illustrates chemical structures of common isocyanate compounds.

Generally, aromatic isocyanates are more reactive as compared to aliphatic isocyanates. This is because the electron withdrawing groups that attached to the isocyanate molecule tends to increase the reactivity of the NCO group. Aromatic isocyanates able to provide good thermal and mechanical properties for SMPU, however, it also suffers from a few inadequacies such as weaker ultraviolet stabilization and lower oxidation. On the other hand, SMPU obtained from aliphatic isocyanates exhibit better resistance to hydrolysis, thermal degradation and light stability. Thus, the use of aliphatic isocyanates is preferred especially when transparency are important for end application (Thakur and Hu, 2017).