SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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SYNTHESIS AND CHARACTERIZATION OF DIFFERENT POLYOL SOFT SEGMENTS IN THE PREPARATION OF PALM KERNEL OIL POLYOL BASED SHAPE MEMORY POLYURETHANE

By

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DECLARATION

I hereby declare that I have conducted, compiled the research work and written the dissertation entitled **“Synthesis and Characterization of Different Polyol Soft Segments in the Preparation of Palm Kernel Oil Polyol based Shape Memory Polyurethane”**. 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

ASTM	American Society for Testing Materials
BD	Butanediol
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermo-Gravimetric
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
HMDI	4,4-methylenebis cyclohexylisocyanate
PU	Polyurethane
PCL	Polycaprolactone
PEG	Polyethylene Glycol
PKO-p	Palm kernel oil-based polyol
PPG	Polypropylene Glycol
T_g	Glass Transition Temperature
T_m	Melting temperature
SMA	Shape Memory Alloy
SMP	Shape Memory Polymer
SMPU	Shape Memory Polyurethane
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction

LIST OF SYMBOLS

°	Degree
θ	Angle
°C	Degree Celcius
%	Percentage
mg	Miligram
min	Minute

SINTESIS DAN PENCIRIAN SEGMEN LEMBUT POLIOL YANG BERBEZA DALAM MENGHASILKAN POLIOL MINYAK ISIRONG KELAPA SAWIT BERASASKAN MEMORI BENTUK POLIURETANA

ABSTRAK

Polimer memori bentuk berasaskan poliuretana (SMPU) sedang dikaji secara aktif untuk digunakan dalam aplikasi perubatan kerana mempunyai sifat bioserasi yang baik dan suhu peralihannya mendekati suhu badan manusia. Dalam kajian ini, beberapa siri poliol (polikaprolaktone diol(PCL), polietilena glikol (PEG), polipropilena glikol (PPG) dan poliol berasaskan minyak isirong kelapa sawit) disintesis dengan 4,4-metilenebis sikloheksilisianat (HMDI), dengan menggunakan 1,4-butanadiol (BD) sebagai penyambung rantai melalui kaedah sintesis pempolimeran pukal. Pengaruh segmen lembut terhadap sifat-sifat mekanikal dan tingkah laku memori bentuk SMPU disiasat. SMPU dianalisis menggunakan teknik analisis yang berbeza seperti spektroskopi infra merah infra merah (FTIR), mikroskop imbasan elektron (SEM), pembelauan sinar (XRD), kalorimetri imbasan perbeza (DSC), analisis termogravimetrik (TGA) dan ujian tegangan. Sifat-sifat SMPU bergantung kepada berat molekul segmen lembut yang rendah dan jumlah kandungan segmen keras dalam matriks segmen lembut. Keputusan menunjukkan bahawa berat molekul segmen lembut yang rendah menunjukkan ciri-ciri mekanik yang lebih baik, manakala berat molekul lembut yang tinggi menghasilkan sifat ketetapan bentuk yang baik kerana struktur hablurya yang tinggi di dalam SMPU. Akhir sekali, SMPU berasaskan PCL menunjukkan sifat tegangan yang lebih baik sedikit berbanding SMPU berasaskan PEG dan PPG.

SYNTHESIS AND CHARACTERIZATION OF DIFFERENT POLYOL SOFT SEGMENTS IN THE PREPARATION OF PALM KERNEL OIL POLYOL BASED SHAPE MEMORY POLYURETHANE

ABSTRACT

Polyurethane-based shape memory polymer (SMPU) is actively investigated to be used in medical applications due to its good biocompatibility and the transition temperature which is closed to the human's body temperature. In this study, several series of polyols (polycaprolactone (PCL), polyethylene glycol (PEG), polypropylene glycol (PPG) and palm kernel oil-based polyol (PKO-p)) were synthesized with 4,4-methylenebis cyclohexylisocyanate (HMDI), using 1,4-butanediol (BD) as the chain-extender via bulk polymerization synthesis method. The influence of the soft segments on the mechanical properties and shape-memory behavior of SMPU was investigated. The SMPU was analyzed using different analytical techniques such as Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), shape memory and tensile testing. The properties of SMPU depend on the molecular weight of soft segment and the amount of hard segment content in soft segment matrix. The result showed that low molecular weight of soft segment show better mechanical properties, whereas the high molecular weight of soft segment produced good shape fixity due to its high crystallinity structure in SMPU. Lastly, PCL-based SMPU showed slightly better tensile properties than PEG-based SMPU and PPG-based SMPU.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Shape memory material is materials that can be recovered to its original shape by an external stimulus, for example, electrical current, heating or photon energy after distortion (Chun et al., 2006). This designation covers an extensive variety of materials such as polymer, ceramic, and metal. Specifically, the unique properties and potential utilization of shape memory materials in electrical, medical, and textile fields have drawn expansive consideration. These materials have excited extraordinary consideration, especially from specialist and researchers due to their capacity to memorize two shapes at different conditions.

Shape-memory materials have the ability to ‘‘hold’’ a permanent shape, be controlled and ‘‘fixed’’ to a temporary shape under particular states of temperature and pressure, and then, relax to the stress-free condition or original shape under electrical, thermal, or environmental command (Liu et al., 2007). The most extensively utilized used shape-memory materials currently are shape-memory alloys (SMA) due to their unique and extraordinary properties. Ni-Ti alloy (Nitinol) is the most widely used shape memory alloys (Ratna and Karger-Kocsis, 2008).

Shape memory alloy (SMA) was first found by Arne Ölander in 1932 (Jani *et al.*, 2014). SMA shows phenomenal properties such as high strength, small size and has found wide specific applications. From that point, the interest for SMAs for outlining and concentrated applications has been growing in different commercial fields, for instance, in biomedical, structures and composites, automotive, aerospace and robotics (Jani et al., 2014). However, they have several disadvantages such as the high cost of assembling, limited recoverable deformation and evident toxic quality (Ratna & Karger-Kocsis, 2008). Such limitations have offered motivation to the advancement of elective materials, especially shape-memory polymers (SMP). Jani et al. (2014) reported that SMP has the advantages of high elastic deformation, low density, minimal cost and potential biodegradability and biocompatibility compared with SMA (Jani et al., 2014). They in like manner have a wide range of application temperatures that can be adjusted and their stiffness also may be tailored.

In 1988, Nagoya Research and Development Centre of Mitsubishi Company has developed Shape memory polyurethane (SMPU). Many researchers have much focus on SMPU because the structure and properties of SMPU can be controlled easily (Wang et al., 2007). Roohpour et al. (2009) stated that polyether based SMPU are currently used in the biomedical application as blood and tissue contacting devices in because of their biocompatibility properties and stability in biological condition.

A segmented SMPU has two phases on its structures, which are the soft segment and hard segment and these both segments cause phase separation (Bonfil *et al.*, 2014). The role of soft segments in the SMPU phase is to switch domain for the fixation of the temporary shape while the function of hard segments is to bind with soft segment through interactions such as hydrogen bonding, dipole-dipole interaction, and van der Waals forces. These interactions would act as physical crosslinking points and affect the SMPU to recover to the original shape after removing the stress (Cha *et al.*, 2014). There are various methods to obtain high-performance SMPU with controlling the molecular structure of soft segment and the hard segment. Modifications of the segment length, hard segment content and the molecular weight of soft segment are introduced to achieve optimum properties (Cho et al., 2004).

SMPU are made by the polyaddition of macro polyols (soft segment) and polyisocyanates (hard segment). The polyisocyanates can be divided into two types, aromatic or aliphatic and often have a molecular weight below than 200 g/mol (Engels et al., 2013). The aliphatic isocyanates are less reactive than aromatic isocyanates. The examples of aliphatic diisocyanates are hexamethylenediisocyanate (HDI), hydrogenated MDI (H_{12}MDI) and isophoronediisocyanate (IPDI). Meanwhile, for the aromatic diisocyanates representatives methylene diphenyldiisocyanate (MDI) and toluene diisocyanate (TDI) (Hearon *et al.*, 2015).

Generally, polyols are separated into two types which are polyester and polyether polyols. Polyester polyol has carboxyl reaction groups while polyether polyol has hydroxyl reaction groups (Lee *et al.*, 2014). The preparation of SMPU from sustainable sources for example vegetable oil-based materials as polyols has been getting expanding consideration due to the financial and ecological concerns (Solanki et al., 2014). PKO-p is alternative crude material for the production of polyurethane polyol based on palm oil. In this study, PKO-p can contribute to increasing the awareness of social responsibility toward the environment to meet the demand for renewable resources and environmentally friendly products. Besides, a few added substances such as chain extender and catalyst may likewise be required during SMPU production, basically to control and modify the reaction and furthermore to complete or modify the final SMPU. The structure of the chain extender has a significantly affect the properties and morphology of SMPU.

The methods for synthesis SMPU can be divided on the several bases of preparation medium either bulk, solution or the sequence of the reactants addition comprising the one-step process and two-step process. A two-step process method often used in the preparation of SMPU due to uniform distribution of the size compared to the one-step method (Cho et al., 2004). Yang et al. (2006) also found that the synthesis of SMPU using two-step process can effectively enhance the properties of SMPU, reduced cost and improve efficiency compared with solution polymerization (Mo *et al.*, 2015). Thus, the bulk polymerization method was selected in this experiment.

1.2 Problem Statement

SMP have tremendous applications in science and pharmaceutical particularly for biomedical devices, which may allow new medical methodology. For instance, current procedure for embedding medical devices regularly requires complex medical procedure took after device implantation. Ratna and Karger-Kocsis (2007) reported smart suture is one of the example medical devices that can develop by thermoplastic elastomer-based SMP (Ratna and Karger-Kocsis, 2007). Most SMPs today have about 100% shape recovery under some condition in the research center but the optimization of mechanical properties for biomedical application and high-performance shape fixity still remain to be solved (Roohpour et al., 2009).

To overcome this problem, SMPU was introduced due to easy modification of the soft segment and hard segment component. SMPU can be designed with an optimum mechanical property and good shape memory properties and with selecting the copolymer compositions based soft phase and hard phase and adjusted the molecular weight of soft segment. HMDI which is aliphatic diisocyanates used as a hard segment in this research can improve the mechanical properties of SMPU. Other than that, the SMPU was expected to have good biodegradable properties for the SMPU would not stay for a long time in the human body and nor require a second surgery to remove medical devices from the human body. The recovery temperature for soft segment must near to human body temperature to make handling of corresponding with medical devices easily. The example of a soft segment that recovery temperature near to human body temperature is PCL which is can be tailored to 37-40°C.

Biodegradable SMPU as biomaterials are reported by several researchers and their properties can be adjusted by proper selection of raw materials. The properties of SMPU extremely dependent on the soft segment structure composed of the polyols. The polyols used in this synthesis include polypropylene glycol (PPG), polyethylene glycol (PEG) and polycaprolactone (PCL). Moreover, the chemical composition of polyol and their molecular weight have an important role to determine the properties of SMPU. The polyols can be incorporated in different concentrations but commonly up to 50-75% of the polyol is used (Cauich-rodríguez *et al.*, 2012). Polyols with a higher molecular weight and enhance the crystallinity of SMPU, hence better mechanical properties. With synthesized the SMPU using different of polyols or soft segment can cause variations in their properties and useful perspective for various medical applications**.**

1.3 Research Objectives

The aim of this research is to produce segmented shape memory polyurethane with good shape memory and mechanical properties. There are some objectives that the project is a concern. The objectives are listed below:

1) To synthesize polyurethane based SMPU via bulk polymerization method
2) To investigate the effect of soft segment molecular weight on the mechanical and shape memory properties of PKO based SMPU
3) To investigate the properties of PKO based SMPU using different types of soft segment on thermal, mechanical and shape memory properties

1.4 Scope of Research

This work is aimed at synthesis SMPU by using two-step polymerization method. In this study, different parameters to synthesis SMPU were investigated, which are the effect of different the type of soft segment used and effect of varying molecular weight of soft segment. The properties of the SMPU were studied using XRD, FTIR, DSC, TGA and SEM.

1.5 Thesis Outline

This thesis is organized into five chapters. Chapter 1 covers the background of the study, problem statement, objectives and scope of the work for this research. In Chapter 2, the literature review of works related to synthesis of SMPU is presented. Moreover, experimental methodology, parameters conducted and characterization methods are laid out in Chapter 3. Chapter 4 focuses on the results and discussion of the research. Lastly, conclusion and recommendations for future work are described in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Shape memory material (SMM)

Shape memory materials are smart materials that can recall and recover substantial programmed deformation upon actuation and be presenting to an external stimulus such as temperature, chemicals, pH, light, a magnetic field and so forth (Zhou and Huang, 2015).The examples of smart materials are Shape Memory Alloys (SMA) and Shape Memory Polymers (SMP). Nowadays, these materials are getting attention from industrial and researchers in terms of further investigation and product improvement (Ghosh et al., 2013).

2.1.1 Shape memory alloy (SMA)

Shape memory alloys are one of the metals that show two unique properties. The first is SMA able to return to the predetermined shape with changing the temperature. The second is the superelastic effect or the pseudoelastic effect. In this state, SMA shows vast recoverable strains (Srivastava *et al.*, 2017). Due to these unique properties, SMA has wide applications such as actuators, transducers, cardiovascular implants and so forth (Srivastava *et al.*, 2017).

Zhou and Huang (2015) reported the most used SMA in the part today is Ni-Ti. It demonstrates different properties according to the activation temperature. The material is easily deformed below the activation temperature and the material becomes much stiffer at the activation temperature. Figure 2.1 shows the phases involved in SMA which are Austenite (high-temperature phase) and Martensite (low-temperature phase). Austenite phase which occurs at high temperature is stronger the Martensite phase (Zhou and Huang, 2015).

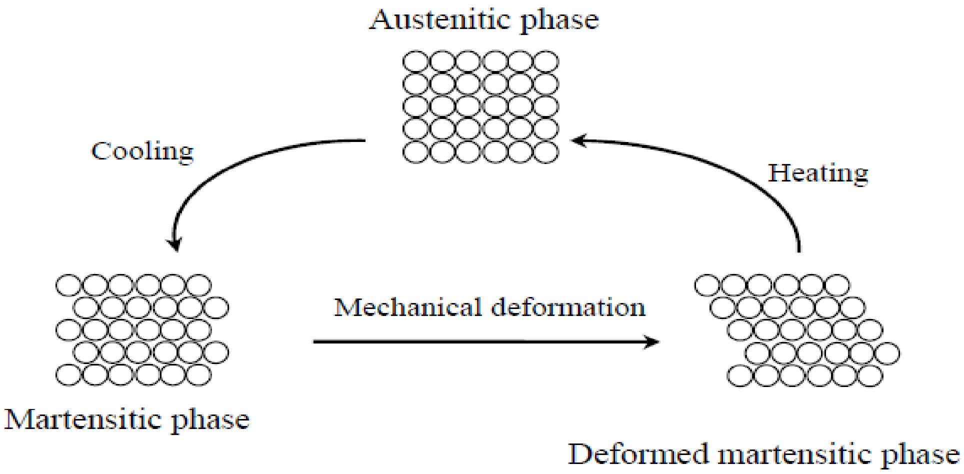


Figure 2.1: Schematic representation of the mechanism of the shape memory alloy (Feina, 2008)

2.1.2 Shape memory polymer (SMP)

Due to limited shape memory materials in several advanced applications such as biomedical applications, shape memory polymer (SMP) was introduced as a valid alternative for shape memory alloy (SMA) (Peponi *et al.*, 2013). The performance of SMP depending on their structures (either thermosets or thermoplastics) and transition temperatures (T_m or T_g). Varying their structures and transition temperature have been reported to show different performances (Sengupta *et al.*, 2007).

Recently, SMP has attracted tremendous attention due to having lots of beneficial than SMA or other ceramics such as high strain recovery after extensive deformation, low density and low recovery stress when contrasted to SMA. Moreover, advantages of lightweight, save cost and simple processibility also have drawn huge attention. SMP have extra favourable circumstances as they can be made biodegradable, non-toxic and have biocompatible properties (Srivastava *et al.*, 2017).

Pilate et al. (2016) also stated SMP have many advantages compared to SMA because of the multitude of desirable qualities such as less demanding handling, high recoverable strain, chemical stability, easy modification, simple processing and degradation rate can be tailored. However, the major disadvantages of the SMP are they have lower tensile strength and stiffness compared to shape memory alloy. Other key constraints incorporate inertness to light, electrical and electromagnetic stimuli accompanied with slow response capacity and low thermal conductivity (Pilate *et al.*, 2016). Table 2.1 was summarized the properties of SMP and SMA.

Table 2.1: Comparison between shape memory polymer and shape memory alloy (Liu et al., 2007)

Property	**SMP**	**SMA**
Density (g/cm^3)	0.9-1.1	6-8
Strain (%)	Up to 800%	Up to 8%
Biocompatibility and biodegradability	High	Not all
Cost	Cheap	Expensive
Processing conditions	<200°C, low pressure	>1000°C, high pressure
Corrosion performance	Excellent	Excellent
Thermal conductivity ($W_m^{-1}K^{-1}$)	0.15-0.30	18

Sengupta et al. (2007) categorized SMP into four types depending on their chemical structure and their transformation temperature which are:

(i) chemically crosslinked glassy thermosets

(ii) chemically crosslinked semicrystalline rubbers

(iii) physically crosslinked amorphous thermoplastics

(iv) physically crosslinked semicrystalline block copolymers.

SMP can be temporarily fixed in a second by application of external pressure. This temporary shape is stable until an appropriate stimulus such as temperature is applied to these materials, which induces the materials to recover to the original shape (Lendlein *et al.*, 2010). Pilate et al. (2016) reported indirect heating such as infra-red irradiation, Joule effect or magnetically actuated nanocomposites also can thermally-triggered the shape memory polymer.

The material must have a permanent domain (chemically or physically crosslinking) and be switching domain (correspond to the external stimulus) in order to achieve shape memory behaviour. The temperature is the most broadly used as external stimulus (Pilate *et al.*, 2016). The nature of switching domains (crystalline or amorphous) also considered as an important factor to determine the transition temperature (T_{trans}). For crystalline materials, melting temperature (T_m) is considered as T_{trans} while glass transition temperature (T_g) for amorphous materials (Peponi *et al.*, 2013).

Liu et al. (2016) stated most SMP are called dual-shape memory polymers due to their capacity to remember and change two unique shapes. Moreover, they show only one transformation, for example, glass transition or melting transition (Figure 2.2). This material can be effectively distorted into any shape at a temperature above T_g because, at this state, SMP has rubbery elastic behaviour. The shape after distortion will fix and remains stable after the materials cooled below T_g. At this stage, the material does not have its rubbery flexibility and becomes rigid. However, the materials can be recovered to the original shape by applying the materials above than T_g (Sokolowski *et al.*, 2007).

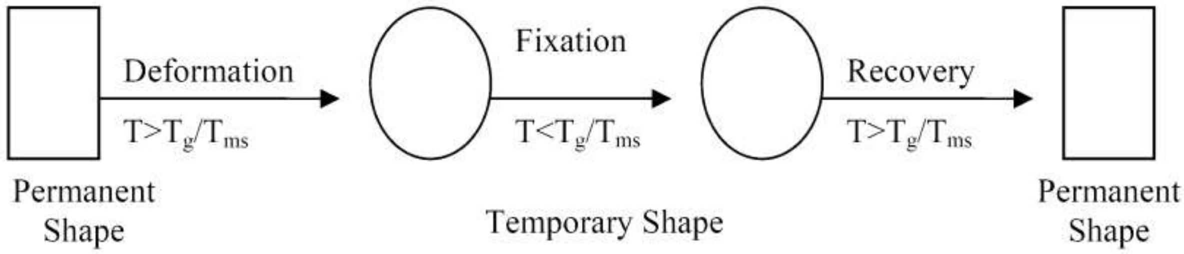


Figure 2.2: Schematic representation of thermally induced shape memory effect (Mondal and Hu, 2006)

Lendlein et al. (2010) stated that SMP is a new material class for innovation in biomedical application. Multifunctional materials can be achieved by combining together the shape memory effect with biodegradability properties in one polymeric system. Srivasta et al. (2017) reported there are many forms of SMP were examined such as polyurethane, isoprene-butadiene-styrene and polystyrene after shape memory behaviour was introduced in polymers. Zhang et al. (2017) also stated polyurethanes, polyamides and polyesters are among the materials used in reported SMP.

2.2 Shape Memory Polyurethane (SMPU)

SMPU haven drawn great attention as compared to other SMP materials and SMA due to their good shape recovery, easy processing, minimal cost and broad temperature range for recovery (Calvo-Correas *et al.*, 2015). Basically, polyurethane is one of the most versatile polymers with an expansive scope of applications. It constitutes a many different of polymeric materials with various properties. They might be thermoplastic or thermoset materials and also may be thermoplastic elastomers that have form virtual crosslinks by microphase separation (Bezuidenhout et al., 2015).

Their fabrication, investigation and characterization of structure-property relations have accordingly been an exceptionally dynamic field of interest both for the industrial researchers and academic for last numerous years (Kausar et al., 2013). They offer exceptional properties for a wide range of applications. SMPU-based thermoplastic polymers with a one of a kind property of showing extensive changes in Young's modulus above and below the T_g (Sokolowski *et al.*, 2007).

SMPU are commonly described by an urea (NHCONH) or carbamate (NHCOO) groups in the polymer chain and also by other groups like amides, ethers and esters (Trinca and Felisberti, 2015). SMPU is blended by reacting three components included of polyols (i.e., polyester or polyether polyols), polyisocyanates and a chain extender, which typically has low molecular weight diols. Nowadays, there is a broad range of polyols, polyisocyanates and chain extenders economically available and this has increase potential outcomes to formulation possibilities for SMPU materials. Due to the natural adaptability in SMPU synthesis, the properties of SMPU can be effectively designed to suit different applications (Mahmood *et al.*, 2016).

Kausar et al. (2013) listed the chemical and structural factors which affected the properties of the SMPU such as:

(i) Chemical structure and the molecular weight of soft segments

(ii) Chemical structure of the diisocyanates

(iii) Chemical structure of the chain extender

(iv) Hard segment/soft segment ratio in the SMPU

(v) The crystallinity of soft segment and the hard segment

(vi) Method of polymerization used to synthesize the SMPU and processing conditions

Currently, there has been expanding enthusiasm for the utilization of uncrosslinked SMPU because of their versatility. They can be utilized in designing materials with various applications, such as biomedical devices and coatings. SMPUs based on polyether and polyester polyols have been examined because of their good mechanical properties and potential for biomedical applications (Trinca and Felisberti, 2015). The properties of SMPU can be adjusted by varying the soft segment content and molecular weight of soft segments (Petrović *et al.*, 2017).

2.3 Raw Materials of SMPU

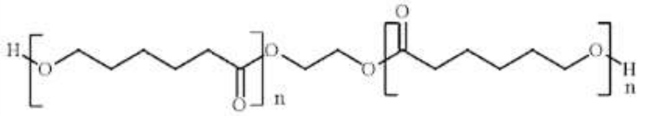
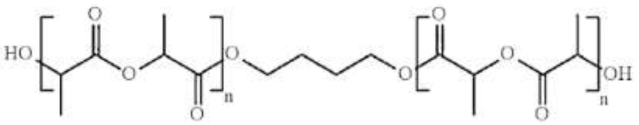
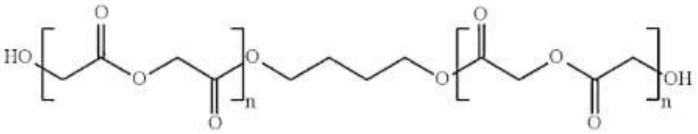
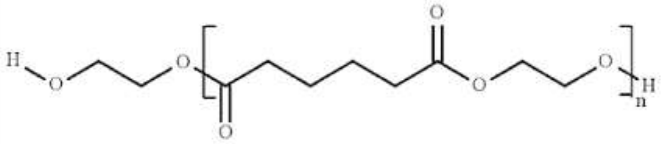
SMPU is one of the versatile polymeric materials that are generally utilized as part of medical, industrial and automotive fields. The SMPU commonly has been synthesized using polyols, diisocyanate and chain extender and because of its simplicity of processability and probability of modifying the compositions, these polymers are broadly utilized (Patel *et al.*, 2015). Sharmin and Zafar (2012) reported the SMPU are formed by specific chemical reaction between polyol and diisocyanate produced repeating urethane groups due to the presence of a chain extender or other additives. Other than that, ester, ether and urea additionally present alongside urethane linkages in SMPU backbone (Sharmin and Zafar, 2012). Several studies have also concluded that polyols, polyisocyanates and chain extender properties such as the molecular weight, chemical structure and functionality can affect the crystallinity of the hard segments (Fazal-Ur-Rehman, 2008).

2.3.1 Polyols

A major part of the SMPU is made out of polyols which decide the properties of the final SMPU. There are numerous sorts of polyols which have made SMPU the most flexible groups of polymeric materials. Basically, these polyols have hydroxyl group which reacts with the polyisocyanate to form SMPU. Normally, polyols are formed having average molecular weight ranges 200-8000 g mol^{-1} with 2 and 8 reactive groups (Randall and Lee 2002). A polyol can be categorized into polyester polyol, polyether polyol, polycarbonate polyol and so forth (Nozaki *et al.*, 2017).

Polyester polyols contain hydroxylic and ester groups in one backbone. This type of polyol is typically prepared by the condensation reaction between glycols. The properties of SMPU likewise rely on the degree of cross-linking and the molecular weight of the starting polyester polyols. The polyester polyols which are highly branched result in rigid PU with good chemical and heat resistance while less branched of polyester polyols provide good greater flexibility and reduce the chemical resistance of SMPU. In case of molecular weight, the high molecular weight polyols produce good flexibility due to long chain polyols while a low molecular weight of polyols provides rigid of SMPU. In addition, polyester-based polyurethanes are more easily attacked by fungi while polyether-based polyurethanes were considered almost completely resistant (Oprea, 2010). However, polyester polyols are susceptible to hydrolysis because of the presence of the esters groups which reduced the mechanical properties (Sharmin and Zafar, 2012). A list of polyester polyols which commonly used for polyurethanes is listed in Table 2.2.

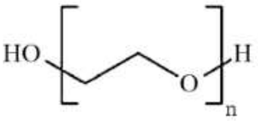
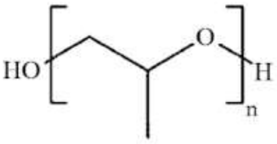
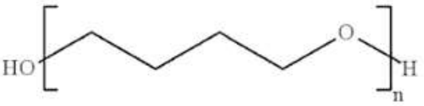
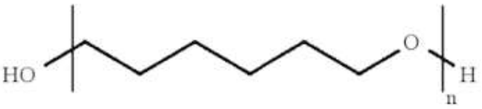
Table 2.2: List of common polyesters polyols and their structures (Cooper and Guan, 2016)

Chemical name	**Structure**
Poly(ε-caprolactone) (PCL) diol	
Poly(D,L-lactide) (PDLLA) diol	
Poly(glycolide) (PGA) diol	
Poly(ethylene adipate) diol	

Mahmood et al. (2016) reported polyester polyols have divided into two structures which are an aromatic and aliphatic structure in SMPU production. Aliphatic polyester polyols are more flexible than aromatic polyesters polyols which commonly used in rigid polyurethane foams. This is because the aromatic structure in aromatic polyesters provides the rigidity of the final properties. In addition, a few of aromatic polyester polyols have drawn huge attention because of less expensive than aliphatic polyesters polyols (Mahmood *et al.*, 2016).

Sharmin and Zafar (2012) stated polyether polyols were replacing the polyester polyols due to their several beneficial for example less expensive, higher hydrolytic stability and ease of handling. However, polyether polyols have higher moisture permeability and the glass transition temperature is low which prevent their extensive application in coating and paints. The examples of polyether polyols are shown in Table 2.3.

Table 2.3: The list of common polyester polyols and their structures (Cooper and Guan, 2016)

Chemical name	**Structure**
Poly(ethylene oxide) (PEO)	
Poly(propylene oxide) (PPO)	
Poly(tetramethylene oxide) (PTMO)	
Poly(hexamethylene oxide) (PHMO)	

Recently, most of the rigid polyurethane is produced from petroleum-based precursors. Even current polyether polyols are frequently based on biomaterial initiators, for example, sucrose or glycerol, they all still use propylene oxide to stretch out the polyol chains to the desired atomic weight. The advantages of petroleum-based precursors as alternative raw materials are increasing the awareness of the environment and availability of the petroleum resources in future. In this manner, there have been numerous reports on incorporating polyurethane foam utilizing bio-based polyols from different vegetable oils, for example, palm, soy castor and different materials, for example, starch, potato, and wheat. The properties and performance of this polyols contrasted with polyether polyols (Septevani *et al.*, 2015).

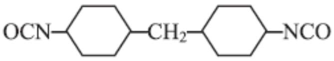
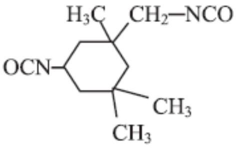
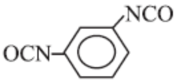
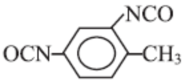
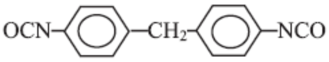
Marcovich et al. (2017) reported bio-polyols used to acquire rigid polyurethane foams in the range of 250–400 mg KOH/g typically have a hydroxyl number. The utilization of vegetable crude materials containing hydroxyl groups, for example, starch, vegetable, oil, castor oil, and so on, makes conceivable to obtain biodegradable polyurethanes (Cauich-rodríguez et al., 2012).

2.3.2 Isocyanates

Isocyanates are fundamental segment required to synthesize the SMPU. They can be aliphatic, aromatic or cycloaliphatic in nature, for example naphthalene 1,5-diisocyanate (NDI), 3,3’- 1,6 hexamethylenediisocyanate (HDI), 4,4’-dicyclohexylmethane diisocyanate (H12MDI) isophoronediisocyanate (IPDI), norbornanediisocyanate (NDI), 4,4’-dibenzyl diisocyanate (DBDI) and 2,2,4-trimethylhexamethylene diisocyanate (TMDI).

Kausar et al. (2013) reported the SMPU properties depended strongly on the structure of a diisocyanate. Table 2.4 shows the chemical structure of diisocyanate commonly used in polyurethane. To synthesize SMPU, both aromatic and aliphatic diisocyanates can be used. Aromatic diisocyanate-based polyurethanes typically have superior thermal and mechanical properties. With the addition of aromatic diisocyanate in the SMPU will form a stiffer polymer chain and increased the melting temperature (Kausar et al., 2013). Sharmin and Zafar (2012) also reported aromatic isocyanates are chosen to produce rigid SMPU. However, SMPU formed from aromatic isocyanates show ultraviolet stabilities and lower oxidative.

Table 2.4: Chemical structure of diisocyanates commonly used in polyurethane (Yilg and Yilg, 2015)

Diisocyanate	Code	Chemical structure
Hexamethylene	HDI	$OCN{-}(CH_2)_6{-}NCO$
trans-1,4-cyclohexyl	CHDI	
Bis(4-isocyanatocyclohexyl)	HMDI	
Isophorone	IPDI	
1,4-Phenylene	PPDI	
1,3-Phenylene	MPDI	
2,4-Tolylene	TDI	
4,4′-Methylenediphenyl	MDI	

2.3.3 Additives

Alongside a polyol and an isocyanate, a few added substances may likewise be required during SMPU production, fundamentally to control and alter the reaction conditions, and furthermore to complete the final product (Sharmin and Zafar, 2012). These incorporate chain extenders, crosslinkers, catalysts, blowing agents, fillers, and others as shown in Table 2.5.

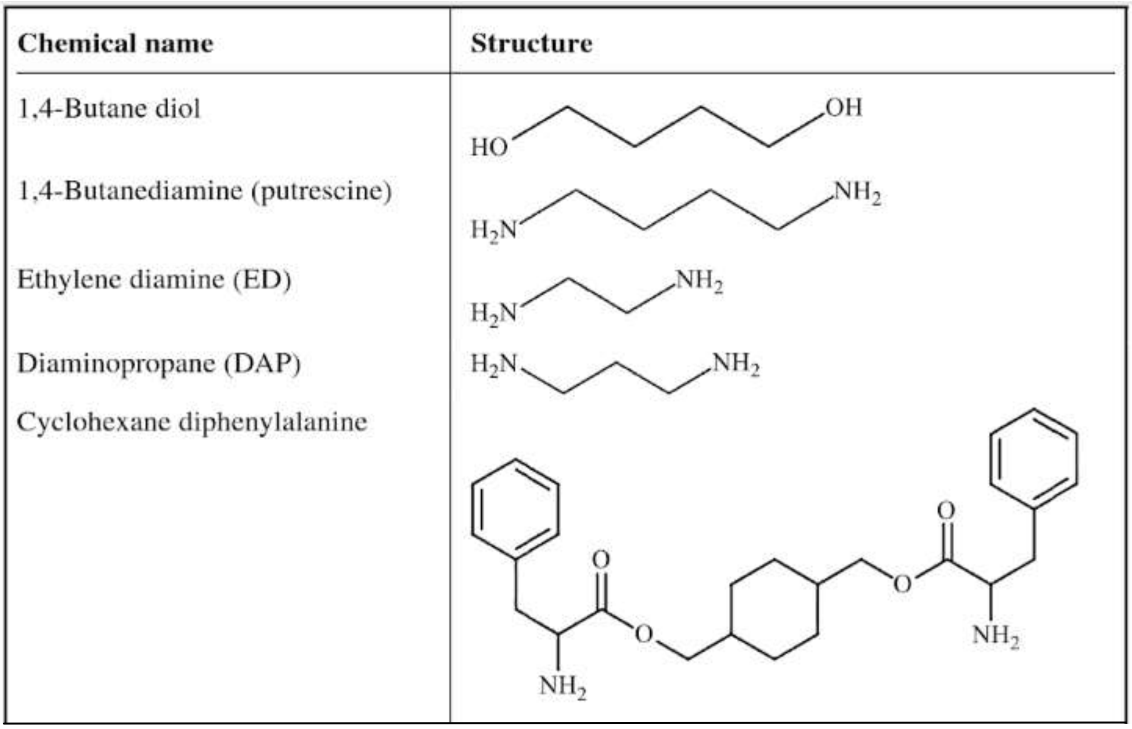
Table 2.5: List of common additives used in polyurethanes (Efstathiou, no date)

Additives	**Required**
Crosslinking agents/ chain extenders	Frequently
Catalyst	Always
Surfactant	Usually
Blowing agents	For foams
Flame retardants	As necessary
Fillers	As necessary
Antioxidants	Frequently
Release agents	For mouldings
Colorants	As necessary

2.3.3.1 Chain Extender

Chain extenders are low sub-atomic weight monomers utilized to bond the prepolymer during the synthesis of SMPU. Any substance compound which is polyfunctional compounds can be classified as cross-linkers while the difunctional compound classified as a chain extender. These cross-linkers and chain extender are normally named as chain extenders. The chain extenders are divided into two classes which are aromatic or aliphatic diols and diamines (Fazal-Ur-Rehman, 2008). Table 2.6 listed the example of chain extender and their chemical structure.

Table 2.6: Chain extender commonly used in polyurethanes (Cooper and Guan, 2016)



Chemical name	Structure
1,4-Butane diol	
1,4-Butanediamine (putrescine)	
Ethylene diamine (ED)	
Diaminopropane (DAP)	
Cyclohexane diphenylalanine	

Based on Table 2.6, 1,4 butane diol or 1,4 BD is the best choice for medicinal applications. This chain extender forming thermoplastic polyurethanes with good mechanical properties and excellent processing conditions (‘Biostability of Polyurethane Elastomers : A Critical Review’, 1938).

2.3.3.2 Catalyst

Catalysts are added during SMPU production generally to enhance the reaction to occur at higher reaction rates in low temperatures conditions. Sharmin and Zafar (2012) reported a number of aromatic and aliphatic amines, organometallic compounds, phenol and alkali metal salts of carboxylic acids are used as catalysts (Sharmin and Zafar, 2012).

The most popular amine catalyst is 1,4-diazabicyclo-[2.2.2]-octane (DABCO), and the most widely used tin catalysts are dibutyltindilaurate (DBTDL) and dibutyltindioctanate. These two types of compounds only make the basis for very specific catalytic systems, which have been developed and which offer a high selectivity with respect to polyol components with different molecular weights and with primary, secondary or tertiary hydroxyl groups, and also with respect to small amounts of water possibly present in polyol feeds (Król, 2007).

2.4 Fabrication of SMPU

The basic components of SMPU are polyol, diisocyanate and chain extender which has low molecular weight diol or diamine. They play a very important role in SMPU. The production of SMPU can be synthesized by one-step or two-step process. In one-step process, all components are mixed homogeneously in to a mixing container before poured the mixtures into a mold. In the two-step process, the polyols were premixed with isocyanate and then chain extender is added at the second stage (Mahmood *et al.*, 2016). Both processes are applicable however there different effect to the final SMPU. Here one-step process and two-step process are described briefly. Figure 2.3 shows the processes of both methods.

2.4.1 One-step polymerization

One-step polymerization is established by simultaneous addition of a polyol, a diisocyanate, and a chain extender stoichiometerically. Polymerization methodology either bulk or solution determine the use of solvent. Solvent is recommended for solution polymerization. Common solvents used in urethane synthesis are dipolar aprotic solvents including N, N'-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and dimethyl formamide (DMF). The reaction mixture is heated above 80-100°C to prepare the polyurethane elastomers. In some cases, catalysts are also recommended especially when aliphatic isocyanates are used (Randall and Lee, 2002).

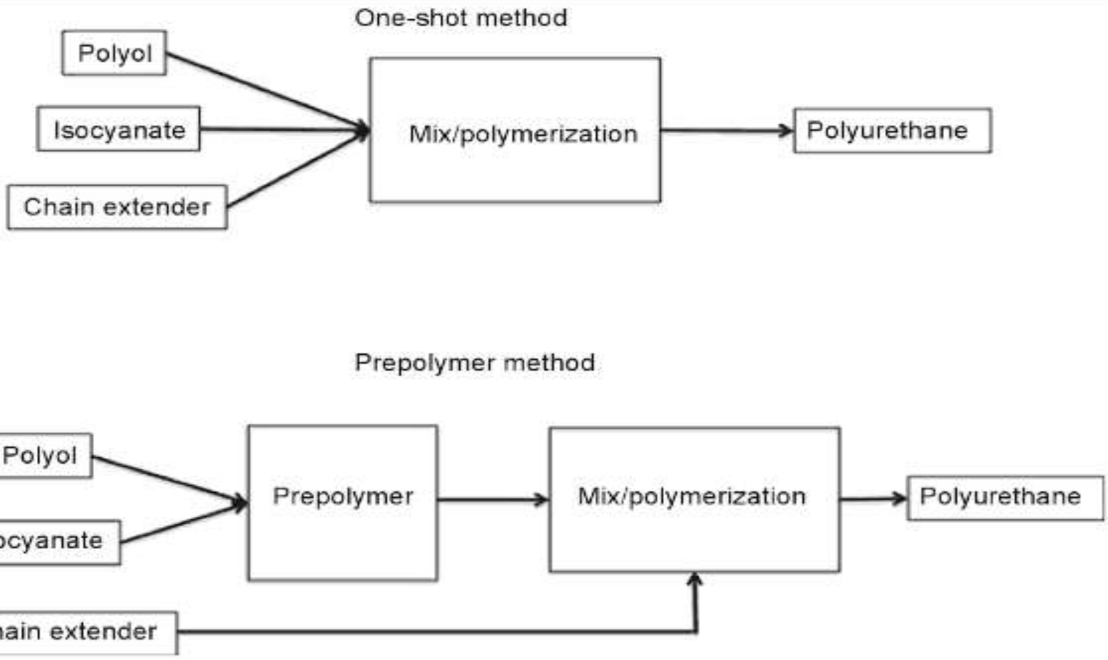


Figure 2.3: Schematic diagram for one-step and two-step process (Cooper and Guan, 2016)

2.4.2 Two-step polymerization

However, two-step synthesis is a more common route for manufacturing the polyurethane. This technique is also termed as the prepolymer method. In the first step, a polyol is reacted with excess of diisocyanate to form a NCO terminated oligomer of high molecular mass known as prepolymer, depending upon the polyol's molecular weight and the ratio between these two reactants. The prepolymer that is formed is usually a sticky liquid, which is easily stored. In the second step, prepolymer is converted in to the final polyurethane by reacting with a diol or diamine acting as chain extender and usually referred to as the chain extension step (Fazal-Ur-Rehman, 2008). This method is also applicable and allows greater control of architecture and composition. The nature and proportions of all components allow the SMPU properties to be controlled (Trinca and Felisberti, 2015). Fazal-Ur-Rehman (2008) stated the structure which made by the two-step method is more systematic than one-step method. This structural regularity determines the better mechanical properties to the polyurethane (Fazal-Ur-Rehman, 2008).

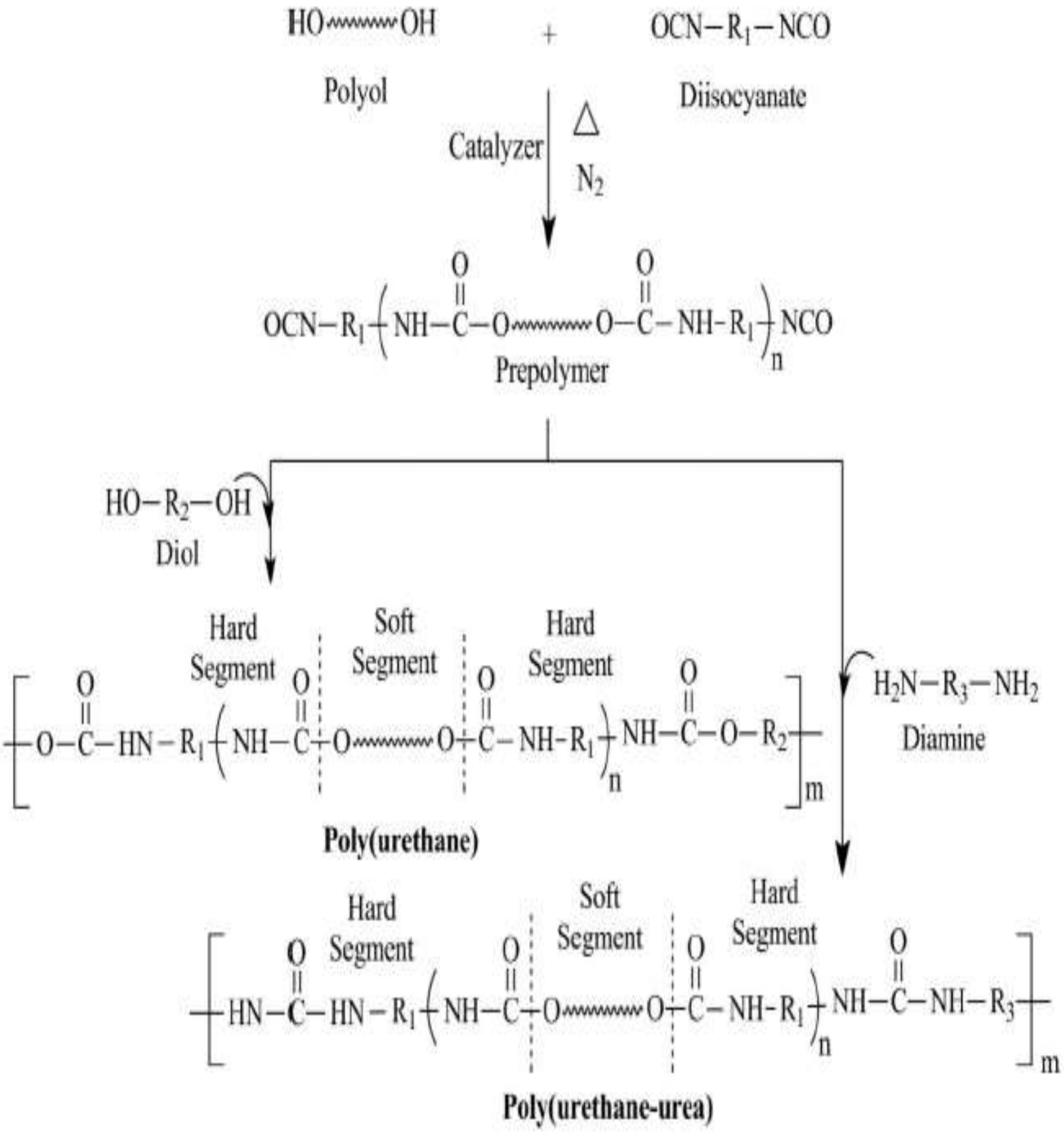


Figure 2.4: Standard two-step reaction to prepare segmented SMPU (Cauich-rodríguez *et al.*, 2012)

2.5 Application of SMPU

Due to outstanding physical, mechanical properties and good biocompatibility, PU has been extensively used in various applications (Patel *et al.*, 2015), including their use as soft foams in furniture, stiff foams for insulation in walls and roofs, thermoplastic polyurethanes for medical products and in the shoe industry as cover layers, and for glues and elastomers for flooring and automotive parts (Mizera and Ryszkowska, 2016). Flexible polyurethane is widely used in a variety of comfort applications such as bedding and seating in the furniture and transportation industries, while rigid polyurethane is an important thermal insulating material in domestic refrigerators and the construction and transportation sectors (Septevani *et al.*, 2015).

Zhang et al. (2016) stated polyurethane has many applications such as fiber, coating, adhesives and smart actuators But its good deformability, low stiffness and tensile strength may limit its application in some field (Zhang *et al.*, 2016). The potential impact of polyurethanes is very strong and promising in several emerging fields such as biomaterials and tissue engineering, optoelectronics, shape-memory materials, conducting polymers etc. Therefore, many studies have been carried out by the chemists concerning their resistance toward heat (Kausar et al., 2013).

Among the SMP, shape-memory polyurethanes (SMPU), play an important role in applications in the biomedical sector due to their biocompatibility, biodegradability, and appropriate mechanical properties in addition to excellent shape-memory properties (Peponi *et al.*, 2013).