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DEVELOPMENT OF PALM KERNEL OIL POLYOL - BASED SHAPE MEMORY POLYURETHANE WITH POLYETHYLENE GLYCOL (PEG) AND POLY CAPROLACTONE (PCL) AS SOFT SEGMENT

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UNIVERSITI SAINS MALAYSIA

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by

NGUYEN HOANG TRINH

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LIST OF ABBREVIATION

SMMs	Shape Memory Materials
SMPs	Shape Memory Polymers
SMAs	Shape Memory Alloys
SMPU	Shape Memory Polyurethane
VO	Vegetable Oil
PKO-p	Palm Kernel Oil polyol
GNP	Graphene nanoplatelet
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
DSC	Differential Scanning Calorimetry Analysis
TGA	Thermogravimetric analysis
FE-SEM	Field Emission - Scanning Electron Microscopy
H-CO	Hydrogen bonded carbonyl group
F-CO	Free carbonyl group
PCL	Polycaprolactone diol
PEG	Polyethylene Glycol diol
HMDI	4,4'-Methylenebis (Cyclohexyl isocyanate)
BD	1,4-butane diol
DBTDL	Dibutyltin dilaurate
MW	Molecular weight
HBI	Hydrogen bonding Index
DPS	Degree of phase separation
SF	Shape fixity
SR	Shape recovery

LIST OF SYMBOLS

Wt%	Weight percentage
^{o}C	Degree Celsius
X_c (%)	Degree of crystallinity
θ_f	Fixity angle
θ_r	Recovery angle
T_g	Glass transition temperature
T_m	Melting temperature
T_{trans}	Transition temperature
ΔH_m	Heat of fusion

PEMBANGUNAN POLIURETANA MEMORI BENTUK BERASASKAN POLIOL MINYAK ISIRONG SAWIT DENGAN POLIETILENA GLIKOL (PEG) DAN POLI KAPROLAKTON (PCL) SEBAGAI SEGMEN LEMBUT

ABSTRAK

Poliuretana memori bentuk (SMPU) adalah antara polimer memori bentuk yang paling penting dan umum, dan kompositnya telah mendapat perhatian disebabkan peningkatan sifat memori bentuk dan mekanikal. Tambahan pula, disebabkan kesedaran terhadap pembangunan mampan, isu-isu alam sekitar, dan pengurangan bahan api fosil, SMPU berasaskan poliol minyak isirong kelapa sawit dan komposit relatif yang diperkuat dengan nanoplatlet grafen (GNPs) telah disintesis dan dicirikan dalam kajian ini. Kedua-dua SMPU dan sampel-sampel komposit telah difabrikasi menggunakan kaedah prapempolimeran dua langkah. Siri SMPU yang berlainan jenis, berat molekul, dan nisbah molar poliol berantai panjang (poli kaprolakton diol (PCL) dan glikol polietilena (PEG)) telah disintesis dan dianalisis. Keputusan-keputusan telah menunjukkan bahawa sampel-sampel PU-PEG (SMPU berasaskan PKO-p dengan PEG sebagai poliol berantai panjang) mempamerkan kebolehtetapan bentuk yang baik tetapi dengan kekuatan tegangan yang rendah disebabkan habluran PEG yang tinggi dan darjah pemisahan fasa (DPS) yang amat tinggi, manakala sampel-sampel PU-PCL (SMPU berasaskan PKO-p dengan PCL sebagai poliol berantai panjang) gagal menunjukkan sifat kebolehtetapan bentuk tetapi mempamerkan kekuatan tegangan dan kelenturan yang baik disebabkan kesan pencampuran fasa. Jenis poliol memberikan kesan yang signifikan terhadap sifat memori bentuk manakala berat molekul memainkan peranan kecil terhadap sifat-sifatnya. Sampel PU-PCLPEG dengan gabungan PCL dan PEG sebagai segmen lembut dapat mengatasi kelemahan-kelemahan sampel PU-PCL dan PU-PEG. Bagi proses pembuatan komposit SMPU, GNP telah difungsikan melalui rawatan asid dan ditaksir menggunakan beberapa analisis (spektroskopi infra-merah, potensi Zeta, miksroskopi imbasan elektron, spektroskopi Raman) sebelum dicampurkan dengan pra-polimer bagi menghasilkan komposit tersebut. Dengan kehadiran kumpulan berfungsi oksigen yang diperkenalkan semasa proses rawatan asid, GNP terawat tersebar dan teragih

dalam matrik PU dengan lebih baik berbanding GNP tanpa rawatan, maka menyebabkan peningkatan sifat-sifat mekanikal, terutamanya terikan tegangan pada titik putus. Komposit SMPU berasaskan GNP terawat (PU-F) mencapai kekuatan tegangan maksimum pada 1% bt GNP terfungsi, iaitu 150% lebih tinggi berbanding SMPU tulen manakala terikan tegangan pada titik putus meningkat sebanyak 1590% berbanding SMPU tulen pada 0.25% bt GNP terfungsi. Sebaliknya, terdapat pengurangan nilai modulus bagi PU-F berbanding SMPU tulen dan nilai modulus meningkat dengan ketara apabila jumlah GNP terawat mencapai 1% bt. Bagi sifat memori bentuk semua komposit, kebolehtetapan bentuk hampir sama dengan SMPU tulen dan kesemua sampel komposit kembali kepada bentuk asal sepenuhnya dengan pemulihan bentuk sebanyak 100%.

DEVELOPMENT OF PALM KERNEL OIL POLYOL – BASED SHAPE MEMORY POLYURETHANE WITH POLYETHYLENE GLYCOL (PEG) AND POLY CAPROLACTONE (PCL) AS SOFT SEGMENT

ABSTRACT

Shape memory polyurethanes (SMPU) is one of the most notable and common shape memory polymer (SMP), and its composites has gained attention due to the enhancement in both shape memory and mechanical properties. In addition, as the awareness of sustainable development, environmental issues, and fossil fuel depletion, palm kernel oil polyol (PKO-p) - based SMPU and its relative composite reinforced with graphene nanoplatelets (GNPs) were synthesized and characterized in this study. Both SMPU and its composite samples were fabricated using two-step pre-polymerization method. A series of SMPU with different type, molecular weight (MW), and molar ratio of long chains polyol (polycaprolactone diol (PCL) and polyethylene glycol (PEG)) was synthesized and analyzed. The results pointed out that PU-PEG samples (PKO-p - based SMPU with PEG as the long chain polyol) exhibited better shape fixity but low tensile strength which is due to the high crystallinity of PEG and extremely high degree of phase separation (DPS) whereas PU-PCL samples (PKO-p - based SMPU with PCL as the long chain polyol) were not able to show shape fixability but exhibited better tensile strength and flexibility due to the effect of phase mixing. The type of polyols attributed significantly to the shape memory properties while the MW had a slight effect on its properties. PU-PCLPEG samples with the combination of PCL and PEG as soft segments overcame the drawbacks of PU-PCL and PU-PEG samples. For the fabrication of SMPU composites, GNPs was functionalized by acid treatment and evaluated using several analyses (Fourier transform infra-red, Zeta potential, Filed-emission scanning electron microscope,

Raman spectroscopy) before incorporating with pre-polymer to produce the composites (varies at 0.25, 0.5, 1.0, 1.5wt% of GNP). With the presence of oxygen-containing functional groups introduced during acid treatment process, treated GNPs dispersed and distributed in polyurethane (PU) matrix was better than the composite with un-treated GNPs, hence results in a remarkable enhancement in mechanical properties, especially the tensile strain at break. Functionalized GNP - based SMPU composite (PU-F) reached maximum tensile strength at 1wt% of functionalized GNP, which is 150% higher compared to that of neat SMPU while tensile strain at break increased 1590% than that of neat SMPU at 0.25wt% functionalized GNP. In contrary, there was a reduction on the modulus of PU-F samples compared with the pristine SMPU, and the modulus was improved significantly when the amount of functionalized GNP reached 1wt%. With regards to the shape properties of all composites, shape fixity was almost similar to that of neat SMPU and all the composite samples recovered completely to their original shape with 100% shape recovery.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Together with the development of science and technology, as well as the higher requirement on various product, the evolution of materials has been a demand. The term “smart material” or “intelligent material” is introduced which refers to the materials that outperform the traditional structural and functional materials (Araújo Mota et al., 2018). Specifically, the smart materials are defined as the materials that possess the capacity to change their physical properties to adapt or respond to specific stimulus such as temperature, pressure, electric field, magnetic field, and so on (Kamila, 2013). Shape memory materials (SMMs) are categorized as a novel of smart materials and they are mainly classified into three types: shape memory alloys (SMA), shape memory polymers (SMP), shape memory ceramics (SMC), and a newly evolving type of SMM is shape memory hybrid (SMH) (Huang et al., 2010, Bothe, 2014).

SMPs are polymeric materials that have capability to be fixed into a temporary shape by applying specific condition, and recovery to their original shape upon the introduction of external stimuli (Schäfer et al., 2018, Hager et al., 2015, Liu and Urban, 2010). In the view of chemical structure, SMPs are considered as phase-separated linear block copolymers consisting of hard segment (HS) and soft segment (SS) (Hu, 2007). While HS acts as a fixed phase to maintain the original shape, SS acts as reversible phase to fix the temporary shape (Leng et al., 2009).

Thermo-responsive SMPs whose the applied external stimulus is heat, have recently received great attention due to their recovery capability at relatively low temperature, easy to modify the transition temperature (T_{trans}) which can be either glass temperature or melting temperature, and applicable for a wide range of applications such as smart fabric, biomedical device, electronic device (Mondal, 2009, Das et al., 2016). In general, the shape memory properties can be programmed as the SMP is heated above the T_{trans} of HS to fix the permanent shape, followed by the deformation of SMP by applying certain condition and cooling the SMP to below the T_{trans} of SS to obtain the temporary shape. The permanent shape will be recovered when the temporary shape is reheated above the T_{trans} of SS (Hu, 2007).

Investigation on SMPs has started in the early 2000's, and afterwards, there are many synthetic polymers are found to demonstrate or possess the shape memory properties (Araújo Mota et al., 2018) such as epoxy resin (Liu et al., 2010), polyurethane (Petrović et al., 2017), polycarbonate (PC) (Wu et al., 2017), polyvinyl alcohol (PVA) (Liu et al., 2018b), polybenzoxazin (Zhang et al., 2019), and so on. Among those polymers, segmented polyurethane (PU) are one of the most notable and common SMPs. Polyurethanes are a class of polymer which the repeating unit comprises of urethane moiety, and the urethane linkage is formed by the reaction between an isocyanate (-NCO) and an alcohol (-OH) (Howard, 2002). The general molecular structure of PU is shown in Figure 1.1.

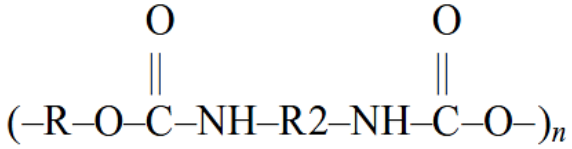

Figure 1.1: The general molecular structure of PU (R: a hydrocarbon containing hydroxyl group, R2: a hydrocarbon chain, n: the number of repeating unit) (Howard, 2002)

Segmented PU – based shape memory polymer are block copolymer that is formed by the HS and SS whose the incompatibility resulted from the difference of chemical and physical properties leading to the microphase separation which highly dependent on the hydrogen bonding interaction, degree of crystallinity, and molecular mass of SS (Calvo-Correas et al., 2016). HS domains formed via interaction between a di-isocyanate and a low molecular mass diol or diamine called chain extender are responsible for controlling the recovery of original shape whereas SS domains built from macro-diol which can be either polyester or polyether diol, play an important role in maintaining the temporary shape (Calvo-Correas et al., 2016, Babaie et al., 2019).

SMPU can be divided into two categories: thermoset SMPU and thermoplastic SMPU (Fu et al., 2015). The covalent crosslinking in thermoset SMPU creates three-dimensional polymeric networks that makes them own excellent thermomechanical characteristics over thermoplastic SMPU such as a higher modulus and faster recovery rate. Nevertheless, they are not able to reprocess, recycle, and the shape recovery is inhibited due to the permanent covalent crosslinking formed during curing process (Chen et al., 2018, Xie et al., 2016, Zain and Zubir, 2016). In contrary, thermoplastic SMPU owns excellent properties such as good processability, recyclability and easy to tailor the desired properties by varying raw materials (Zhou et al., 2018).

In addition, segmented SMPU inherits attractive properties from segmented PU such as high processability that enable for industrial scale production (Petrović et al., 2017), light weight, and low cost (Gupta and Kim, 2019). Hence, SMPUs have found their role in wide range of applications, especially sensor and actuator (Petrović et al., 2017). However, the major drawback of SMPs in general is relatively low

mechanical properties, especially modulus that leads to low recovery force (Babaie et al., 2019, Fonseca et al., 2013).

Most of the precursors used to synthesize polymer, are derived from non-renewable petroleum resources; therefore, the use of petroleum – based polymers contribute to the reduction of fossil fuel resources which cause the raise of fuel cost. In addition, the environmental issues such as water pollution due to the large amount of non-degradable waste is increasing day by day, which has become the utmost concern (Zhang et al., 2017). Hence, the search for resources that are renewable and able to replace the role of petroleum in synthesis of polymer, as well as having less impact to the environment, has accelerated.

Vegetable oil (VO) has gained great attraction from both academic and industrial sector since it is considered as the most abundant, low-cost, non-toxic, and biodegradable renewable resources (Sharmin et al., 2015). VO comprises of triglycerides with three long molecular chain fatty acids (Miao et al., 2014). Moreover, VO – based polyols can be produced by modifying the structure of VO in order to introduce the hydroxyls groups (-OH) (Alagi et al., 2016). Thus, there are many VOs have been employed to synthesize PU, for example, castor oil (Ionescu et al., 2016, Zhang et al., 2014), rapeseed oil (Kurańska and Prociak, 2016), soybean oil (Alagi et al., 2018), andiroba oil (da Silva et al., 2018), palm oil (PO) (Ahmad Zubir et al., 2018, Ng et al., 2017), palm kernel oil (PKO) (Septevani et al., 2015, Zulkifli and Amin, 2016) etc.

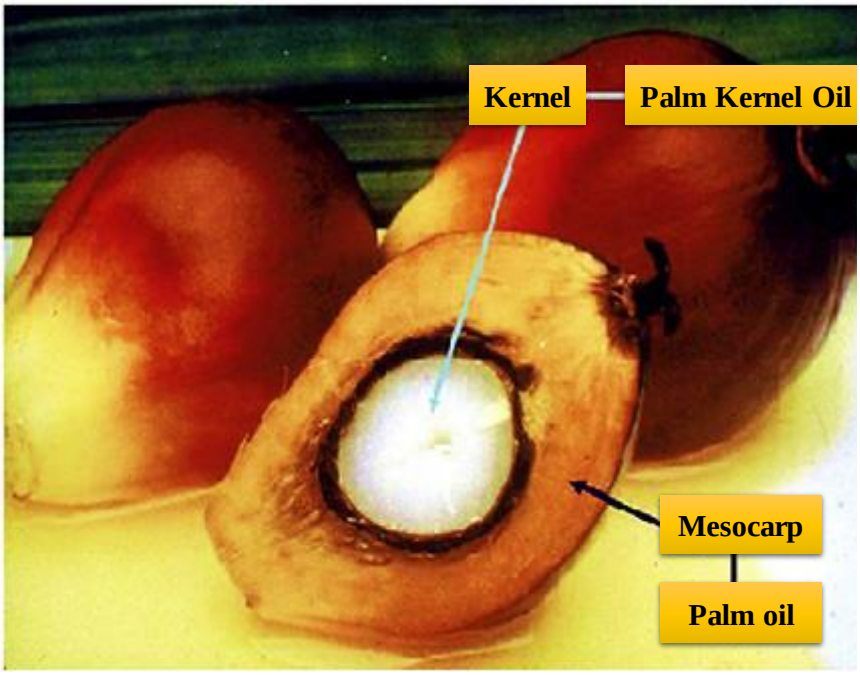

Figure 1.2: Cross section of fresh oil palm fruit (Ahmad et al., 2019)

Malaysia is one of the world largest palm oil manufacturers; therefore, oil palm crop has been the most important crop and played an essential role to the economic development of this country (Awalludin et al., 2015). There are two types of oils generated from the oil palm fruit: PO is obtained from the mesocarp fiber while PKO is derived from the kernel seed of the fruit (Septevani et al., 2015) (Figure 1.2). PKO - based polyester polyol (PKO-p) is a commercial product that is formed from the reaction between PKO and polyhydric alcohol (Badri, 2012). There is few published papers reported on the synthesis of PU from PKO-p (Zulkifli and Amin, 2016, Wong and Badri, 2012, Septevani et al., 2015), and none of those studies has reported on the potential of PKO-p for the synthesis of SMPU.

In order to improve the mechanical properties with the use of VO – based polyol in the synthesis of SMPU to form a “greener composite”, the reinforcements are incorporated into the bio-based polymer matrix (Zhang et al., 2017, Mosiewicki

and Aranguren, 2013). There is a wide range of nanosized-reinforcements for polymer such as nanoclay (Cao and Jana, 2007, Zubir et al., 2012), carbon nanotube (CNT) (Paik et al., 2006), graphene (Kim et al., 2015, Park et al., 2014), graphene nanoplatelets (GNPs) (Kumar and Purohit, 2019), and so on.

In recent year, graphene nanoplatelets (GNP) which is comprised of a few mono layer graphene stack (Wang et al., 2015) has drawn much interest among researchers as a novel reinforcement for polymer composites (Dai et al., 2016, Kausar, 2016). As compared to CNT and mono-layered graphene, GNP can be produced at a large scale with cost efficiency due to the simple manufacturing process and abundance of low-cost natural graphite sources (Li et al., 2007, Wang et al., 2016a). In addition, GNP also inherits attractive properties of monolayer graphene such as high aspect ratio, high modulus, good thermal and electrical conductivity (Kausar and Ur Rahman, 2016, Kuan et al., 2018). Nevertheless, GNP with very high surface area can agglomerate when incorporated with polymer due to the interplanar π-π stacking interaction, as well as weak bonding with the polymer chain, which diminish the ability to obtain a homogenous distribution composite (Chatterjee et al., 2011, Manafi et al., 2014). Hence, the modification of the GNP surface by introducing functional groups, can be useful to overcome the problem associated with filler distribution (Ahmadi et al., 2015).

1.2 Problem Statement

The awareness on the environment issues and sustainable development for the next generations have risen significantly in the era of 2000's, resulting the searches for other renewable resources that can replace efficiently the role of fossil resources, especially in terms of petroleum – based products (Mosiewicki and Aranguren, 2013).

In recent years, there are few reports on polyurethane (PU) obtained from the palm kernel oil polyol (PKO-p) (Daud et al., 2014, Badri, 2012, Wong and Badri, 2012, Zulkifli and Amin, 2016), which suggests the potential of PKO-p in the synthesis of PU. However, in the effort to obtain PU with higher performance such as shape memory behavior, the incorporation of long chain polyols and PKO-p to form soft segments is less considered.

Phase separation, resulting from the thermodynamic incompatibility of SS and HS, plays a vital role in shape memory properties of SMPUs (Erekkath and Sreejalekshmi, 2018, Peponi et al., 2013). Moreover, the type and the molecular weight (MW) of SS is one of the important factors affecting the degree of phase separation (DPS) (Petrović et al., 2017, Prisacariu, 2011b). Hence, the effect of different type of polyols (ester polyol or ether polyol) with various MW on the shape memory behaviors of PKO-p-based SMPU is worth to evaluate. In this study, polycaprolactone (PCL) – an ester polyol and polyethylene glycol (PEG) – an ether polyol were employed as the component of SS. Additionally, according to Ahmad et al (2012) and Firdaus et al (2015), PEG - based SMPU exhibits good shape memory effect (SME) but the mechanical properties was limited due to its brittleness (Ahmad et al., 2012, Firdaus et al., 2015). In contrary, PCL is known as a flexible polyol, consequently PCL-based SMPU possesses a good elastomeric mechanical properties (Ahmad et al., 2012, Cakić et al., 2014). Thus, the combination of PEG and PCL as the soft segment can be lucrative and the variation of PEG/PCL molar ratio may be the key to optimize the properties of SMPU in terms of shape memory and mechanical properties.

In the effort to further enhance the mechanical properties, as well as utilization of VO – based polyol in synthesis of SMPUs, “greener composite” has gained great

attention (Zhang et al., 2017, Mosiewicki and Aranguren, 2013). Graphene nanoplatelets (GNP) is a prospective nano-reinforcement filler in fabricating composites. However, to obtain a good composite, a surface modification of GNP should be conducted and acid treatment seems to be the simplest method to improve the dispersion and distribution of GNP in the PU matrix (Zhang et al., 2003, Thi Mai Hoa, 2018, Saito et al., 2002). Last but not least, in the best of our knowledge, there is still lack of studies have done on the SME of PKO-p - based SMPU, as well as PKO-p - based SMPU composite so far.

1.3 Research Objectives

The objectives of this study are listed as below:

i. To investigate the effect of PCL and PEG with different molecular weights (2000 and 4000 g/mol) on the shape memory and mechanical properties of PKO-p - based PU.
ii. To synthesize and characterize the thermal, mechanical and shape memory properties of PKO-p - based SMPUs with the combination of PCL and PEG polyol as mixed soft segment.
iii. To examine the effect of varying different molar ratio of PCL and PEG as soft segments on the shape memory and mechanical properties of PKO-p - based SMPU.
iv. To functionalize GNP via acid treatment, fabricate and characterize the properties of GNP – based SMPU composite.

1.4 Scope of Research

In this study, firstly, palm kernel oil– based SMPU was fabricated via two-steps bulk polymerization process using PCL, PEG, and PKO-p as multiple block soft segment whereas 4,4'-Methylenebis (Cyclohexyl isocyanate) (HMDI) and 1,4-butane diol (BD) act as hard segment. The use of PKO-p whose molar ratio in all SMPUs was maintain at 0.2, is due to the concern about environment. The shape memory and mechanical properties of synthesized SMPUs were investigated and optimized by varying the long chain polyols in the soft segment, as well as their molecular weight.

Secondly, the incorporation of GNP into SMPU matrix to enhance the mechanical properties of SMPUs was conducted. In addition, GNP was further functionalized using acid treatment so as to improve the dispersion ability of the reinforcement in the matrix. The functionalization was taken place in a two-neck ground bottom flask at a specific temperature and period of time. Treated GNP after that was characterized by employing Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and Thermogravimetric analysis (TGA) to prove that the functionalization was successful. GNP-based SMPU composite were fabricated by incorporating either pristine GNPs or treated GNPs with pre-polymer in an internal mixer, follow by hot pressing to obtain a 0.5 mm – thin sheet. The SMPU and composite samples were examined using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential Scanning Calorimetry Analysis (DSC), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), Tensile Test, and Shape Memory Test.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Smart material can be defined as a material that possesses ability not only to offer reversible response when surrounding environment changes but also to contribute useful response to adapt those changes (Hu, 2007). Base on that, shape memory material (SMM) is categorized as a novel class of smart materials due to their capability to recover original shape upon application of right external stimuli. This behavior is also known as shape memory effect (SME) and the stimulus can be heat, electricity, magnetic field, light, pH, and so on (Huang et al., 2012, Chatterjee and Naskar, 2017). The history of the development of SMMs has started since SME was first investigated in an gold–cadmium alloy in early 1932 and their applications has been expanding in many fields such as civil structure, aerospace engineering, and biomedical devices until now (Liu et al., 2014, Song et al., 2006a, Dhanasekaran et al., 2018, Zhao et al., 2018).

SMMs are classified into shape memory alloys (SMAs), shape memory polymers (SMP), shape memory ceramics (SMCs), and a newly evolving type of SMMs is shape memory hybrid (SMH) (Huang et al., 2010, Bothe, 2014). SMA and SMP are conventional SMMs that have been used in a widest range of applications (Hu, 2007). Nevertheless, SMPs have gained great attraction in recent years due to lightweight, cost effective, easy to process (Ōtsuka and Wayman, 1998) and ability to use various stimuli to activate the SME as compared to SMAs.

2.2 Shape memory polymers (SMPs)

Shape memory polymers are defined as polymers which have capability to memorize its permanent shape, be programmed to a temporary shape by applying specific circumstances, and after that the material is able to recover to the original shape upon introduction of the right external stimulus that can be cover a wide range such showed in Figure 2.1 (Hager et al., 2015, Liu and Urban, 2010).

Shape memory effect (SME) in polymer was first mentioned by L. B. Vernon in a United States patent about a thermoplastic synthetic resin being able to return to its original shape by heating in 1941 (Liu et al., 2007). After the handling of cross-linked polyethylene into heat shrinkable tubes and films in the 1960s, the importance of shape memory polymers (SMPs) was recognized (Rainer et al., 1964) and they have accelerated research attention from both academic and industrial fields from the 1980s up to now. SMPs have been utilized in a wide range of real world applications such as functional textiles (Mondal and Hu, 2007c, Xie et al., 2010), electronic devices (Liu et al., 2018a, Zarek et al., 2016), biomedical devices (Ward Small et al., 2010, Razzaq et al., 2019), and aerospace applications (Sokolowski and Tan, 2007, Liu et al., 2014).

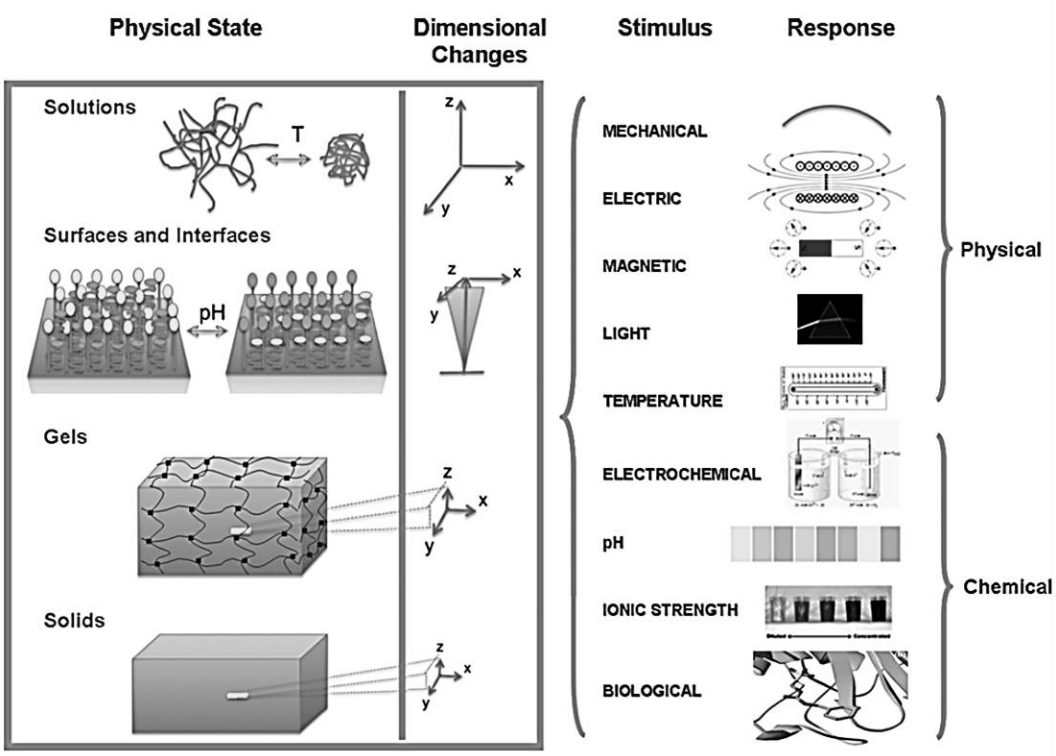

Figure 2.1: Graphic illustration of dimensional changes in SMPs upon different stimuli (Liu and Urban, 2010)

2.2.1 Type of shape memory effects (SMEs)

SMPs have similar characteristics to SMAs; however, their physical principles are quite different in basic. The SME of a SMA comes from the application of a plastic deformation at the temperature that it turns into elastic by heating, and this phenomenon allows SMAs to return to its permanent shape. In case of SMPs, they depend on a transition temperature (T_{trans}) around which a SMM changes its state (Chatterjee and Naskar, 2017), to operate a shape changing. In addition, the modulus of SMAs increases with heating while the modulus of SMPs decreases when heat is applied over transition temperature (Monkman, 2000).

2.2.1(a) One – way SME

One – way SME of SMPs is a behavior that the external stimuli triggers changes, from a temporary shape to a permanent shape, demanding the introduction of an external mechanical interference to establish again the temporary shape (Pandini et al., 2013). In another words, SMPs classified in one-way SME are able to remember only one particular shape. SMPs with one-way SME can be utilized to applications that need only a single SM cycle to achieve the desired performance (Huang et al., 2013).

The basic process of polymer SME has 3 steps. Firstly, heat is applied to the SMP upon a transition temperature caused in softening of the polymeric material. Secondly, an external force is applied to deform SMP. Finally, the SMP is cooled down without removing the load. The temporary shape is obtained when the load is removed. After that, reheating the temporary shape of SMP to transition temperature, and the original shape of SMP is recovered when no load is introduced on it. This process can be known as dual-shape memory effect (Erkeçoğlu et al., 2016). Most of the typical SMPs perform one-way SME (Basit et al., 2013). From engineering practice viewpoint, one-way SME is still the SME used the most because of their flexibility, versatility, applicability and they can offer reliable performance (Hu, 2014). The one-way SME is illustrated briefly in Figure 2.2.

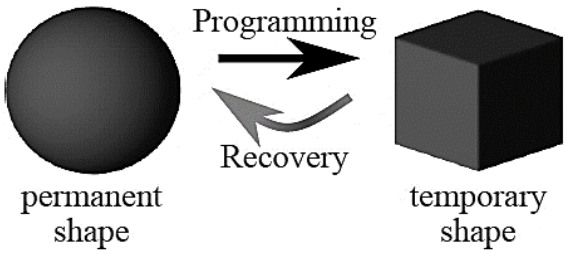

Figure 2.2: One – way SME (Bothe, 2014)

2.2.1(b) Two – way SME

In comparison with one-way SME, SMPs that possess two-way SME, exhibit 2 different shapes: one at high temperature and the other at low temperature during a controlled thermo program. SMPs can be programed to behave in those conditions with or without applying external force so as to "memorize" their shape at high temperature while upon heating and "forget" their low temperature shape instantly (Chatterjee and Naskar, 2017). This characteristic property makes two-way SME owns advantage over one-way SME for applications that require reversible shape changing such as reversible actuator (Westbrook et al., 2011). The differences between two-way and one-way SME is revealed in Figure 2.3.

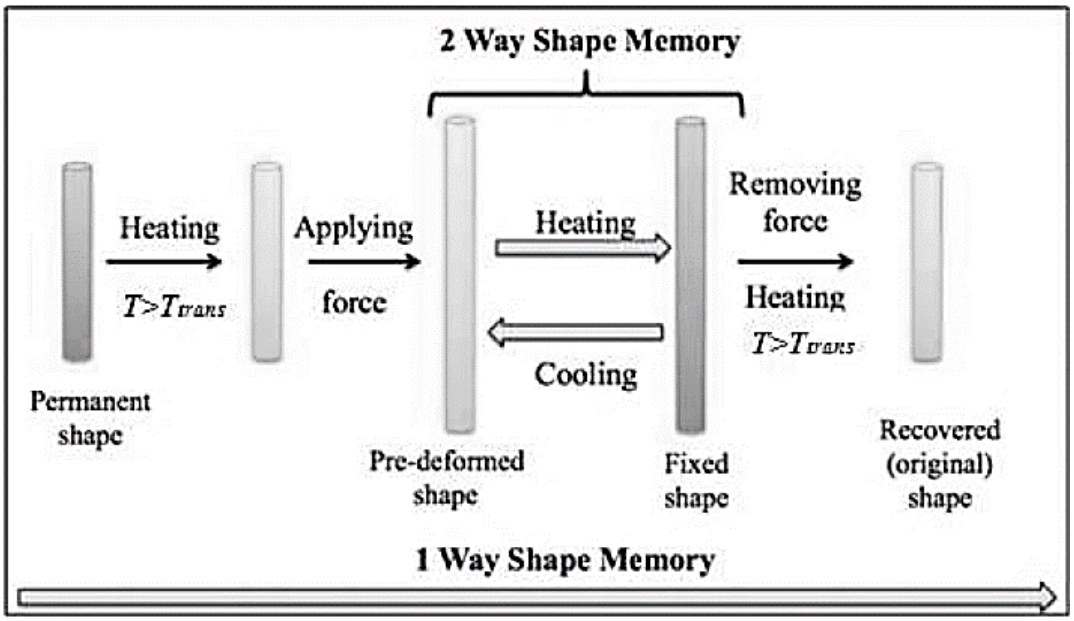

Figure 2.3: Comparison between two-way and one-way SME (Erkeçoğlu et al., 2016)

2.2.1(c) Triple and multiple SME

Multiple SME arises from the phenomena that a SMP with the one-way SME has ability to perform at least one intermediate shape throughout recovery process (Wu

et al., 2013). SMP has triple – way SME if it has only one intermediate shape which is attributed to a multiphase polymer network containing as a minimum of two separated domains. At the first transition temperature, SMP switches between its temporary shapes, and after that it turns back to the permanent shape at another higher temperature (Chatterjee and Naskar, 2017).

2.2.2 Architecture of SMPs

Architecture of SMPs are mostly dual-shape, one is an original shape (permanent shape), and the other is a deformed shape (temporary shape), which is consequent on a combination of molecular architecture of polymeric material and a specific programming process. A special chemical architecture is required to achieve the SME. This architecture involves net points and molecular switches being responsive to the external stimuli. In this case, SMP is considered as a copolymer whose hard segments act as fixed phases and soft segments act as reversible phases (Leng et al., 2009).

While the net points that can be originated from either chemical or physical cross-links, control the permanent shape and offer the stability of dimension to the SMP network, the molecular switches that can be either amorphous or semi-crystalline, response to maintain the temporary shape and shape recovery upon a defined and programmed external stimulus (Hu et al., 2012). Based on the molecular mechanisms, Hu and Chen (2010) proposed a general three-dimensional SMP architecture as shown in Figure 2.4.

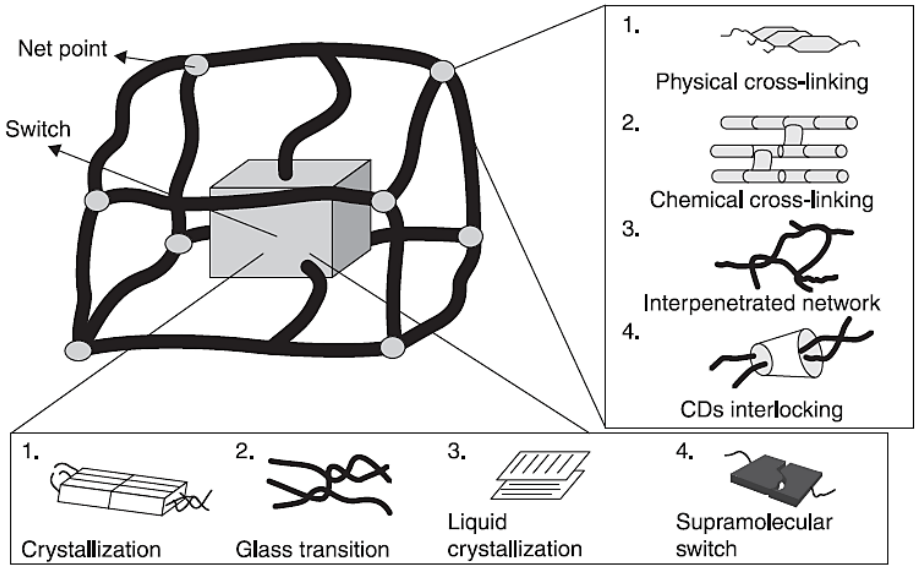

Figure 2.4: The general architecture of SMPs (Hu and Chen, 2010)

2.2.3 Categories of SMPs

Based on the nature of net-points and the thermal transition resulted from the switching components, thermal-induced SMPs can be classified into four different categories (Hu et al., 2012):

i. Chemically cross-linked net-points and amorphous switching domains (T_{trans} = glass transition temperature, T_g).
ii. Chemically cross-linked net-points and semi-crystalline switching domains (T_{trans} = melting temperature, T_m).
iii. Physically cross-linked net-points and amorphous switching domains (T_{trans} = glass transition temperature, T_g).
iv. Physically cross-linked net-points and semi-crystalline switching domains (T_{trans} = melting temperature, T_m).

The first two groups belong to the thermoset SMPs. They have covalently interconnected structures which determine the permanent shape of SMPs. The last two groups belong to the thermoplastic SMPs whose the fundamental mechanism of the SME that induced by thermal trigger, is resulted from the creation of the phase-separated morphology. One phase offers the physical cross-links whereas another phase performs as a molecular switch (Leng et al., 2011).

In addition, SMPs can be also separated into two categories based on the transition temperature of the switching components. In the case of the SMPs based on a glass transition, the temporary shape is fixed at a low-temperature, which is resulted from the freeze of the micro Brownian movement belonging to the network chains. The temporary shape is maintained and the strain energy is stored until the switching domains are activated upon heating at or above T_g. Glass transition is always a wide temperature range. As regards of the SMPs based on a melting point, the temporary shape is obtained from the crystallization of the switching components at low temperature, and after that the permanent shape is recovered at or above T_m (Hu, 2007). Figure 2.5 represented the classification system of existing SMPs.

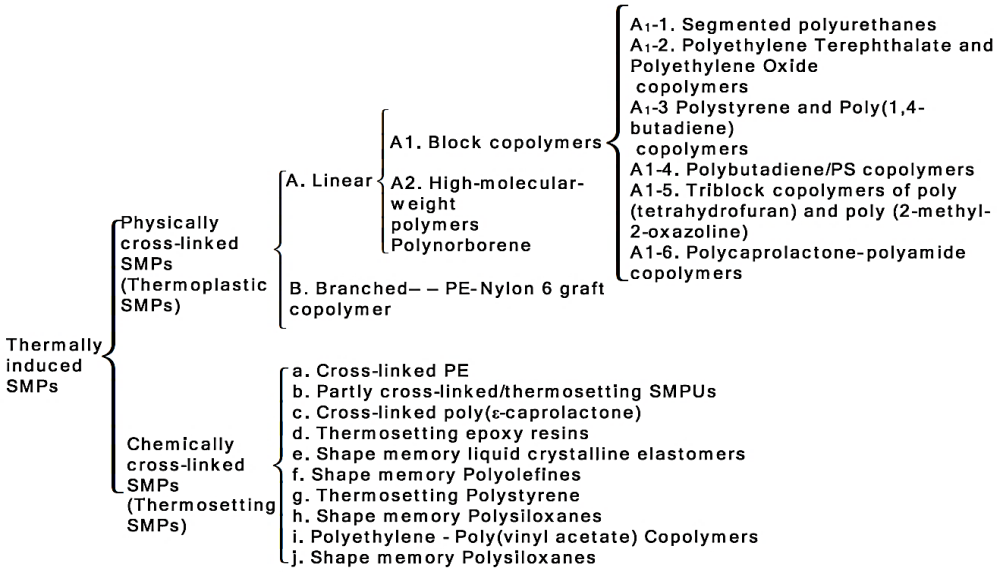

Figure 2.5: Schematic structural classification of SMPs (Leng et al., 2011)

2.3 Shape memory polyurethanes (SMPUs)

Shape memory polyurethanes (SMPUs) are the most popular class of SMPs (Kim et al., 2015). SMPUs have captivating advantages over other types of SMPs such as easy to process, low cost of raw materials and processing, recovery strain can be up to 100%, biocompatibility, and the most importance that their properties can be easily tailored by changing the molecular structure and molecular weight of soft segment, type of hard segment, and the ratio of soft and hard segment (Kim et al., 2015).

Mitsubishi Heavy Industry (MHI) introduced SMPUs with the glass transition in range from -30^{o}C to 100^{o}C, and they could be fabricated by traditional processes such as extrusion, injection molding, and solution coating (Gordon, 1993). Since then, a number of SMPUs have being developed up to now in both research and industrial fields. The recent researches about SMPUs and their applications were briefly listed in Table 2.1.

Table 2.1: Recent researches and applications of SMPUs

Applications	**References**
Smart fabric	(Lin et al., 2007, Cho et al., 2004, Mondal and Hu, 2007a)
Electronic device	(Deng et al., 2015)
Biomedical device	(Muschalek et al., 2017, Zhuo et al., 2018, Huang, 2010, Petrović et al., 2017)
Smart actuator	(Wang et al., 2017b, Cho et al., 2005, Mahapatra et al., 2014, Paik et al., 2006)

2.3.1 Structure and mechanism of SMPUs

SMPUs fundamentally consist of two separated-phases that are soft and hard segment (Jeong et al., 2000). This unique characteristic architecture resulted from the

thermodynamic immiscibility between these two phases (Huang et al., 2012). The overall structure of SMPUs is illustrated as Figure 2.6.

Long chain polyol forms the soft segment or reversible phase that acts as switch domains, exhibiting a phase transition temperature, T_{trans} (glass transition or melting transition temperature). The temporary shape is obtained after cooling down the SMPU from this transition temperature (Lin and Chen, 1998b).

Hard segments form the net-points that can be crystalline structure, covalent crosslinking, or incorporation of interpenetrating networks (Thakur and Hu, 2017, Lin and Chen, 1998a). These net-points link with soft segments by interactions such as hydrogen bonding and dipole-dipole interaction (Fonseca et al., 2013) to create fixed phases that is responsible to the shape recovery. According to Lee et al (2001) and Yang et al (2003), the weight percentage (wt%) of hard segment affects to the shape recovery ability of SMPUs. The optimal hard segment content is in range of 30-45wt% at which the shape recover value can achieve 80-95%. If the hard segment content is too low, about 20-25wt%, the shape recover effect cannot obtain; however, SMPU with high hard segment content, above 50wt%, becomes brittle and SME is lost (Lee et al., 2001, Yang et al., 2003).

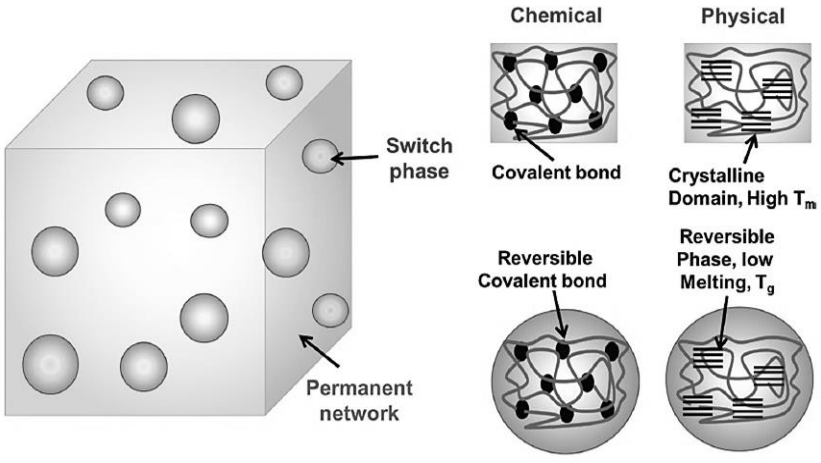

Figure 2.6: General architecture of SMPUs (Thakur and Hu, 2017)

SMPUs can also be classified into two categories: thermoset SMPUs and thermoplastic SMPUs (Fu et al., 2015). Their general structure is represented in Figure 2.7. As can be seen from that figure, the covalent crosslinking in thermoset SMPUs creates three-dimensional polymeric networks that make thermoset SMPU possesses excellent thermomechanical properties over thermoplastic SMPU such as a higher modulus, a faster shape memory effects rate. Nevertheless, they cannot reprocess, and recycle (Chen et al., 2018, Xie et al., 2016).

In contrary, thermoplastic SMPUs whose hard segments act as the physical crosslinking while soft segments act as reversible phases, are flexible, easy to reprocess, and recycle (Zheng et al., 2016). Moreover, they own characteristic properties such as good processability, various precursor materials, biocompatibility, and biodegradability. However, the major problem of thermoplastic SMPUs is relatively low thermomechanical properties that restrict to expand their application in engineering area (Zhou et al., 2018).

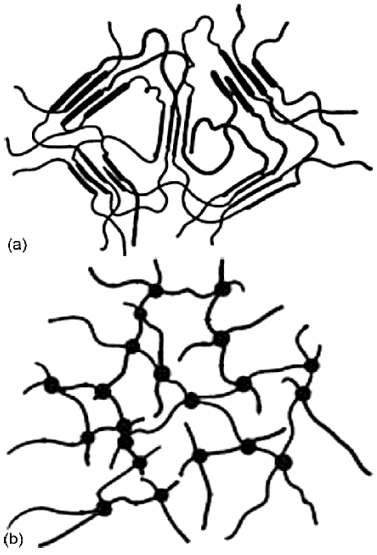

Figure 2.7: Structure of (a) thermoplastic SMPU, and (b) thermoset SMPU (Fu et al., 2015)

A typical thermally induced SME of SMPUs is represented in Figure 2.8. When SMPU is heated above T_{trans} of hard segment, the soft and hard segment become flexible and SMPU changes from a glassy state to an elastic rubber state where it can be deformed elastically under an applied load (Yang et al., 2007). When the deformed PU is cooled down below the T_{trans} of reversible phase without releasing the applied load, the temporary shape is obtained because of the crystallization process that freeze the deformation even though the load is released after that (Hu, 2007, Lin and Chen, 1998a). The permanent shape will be recovered by heating the SMPU above T_{trans} of hard segment again at which the physical cross-linked bonding between the hard segments is destroyed (Zain and Zubir, 2016).

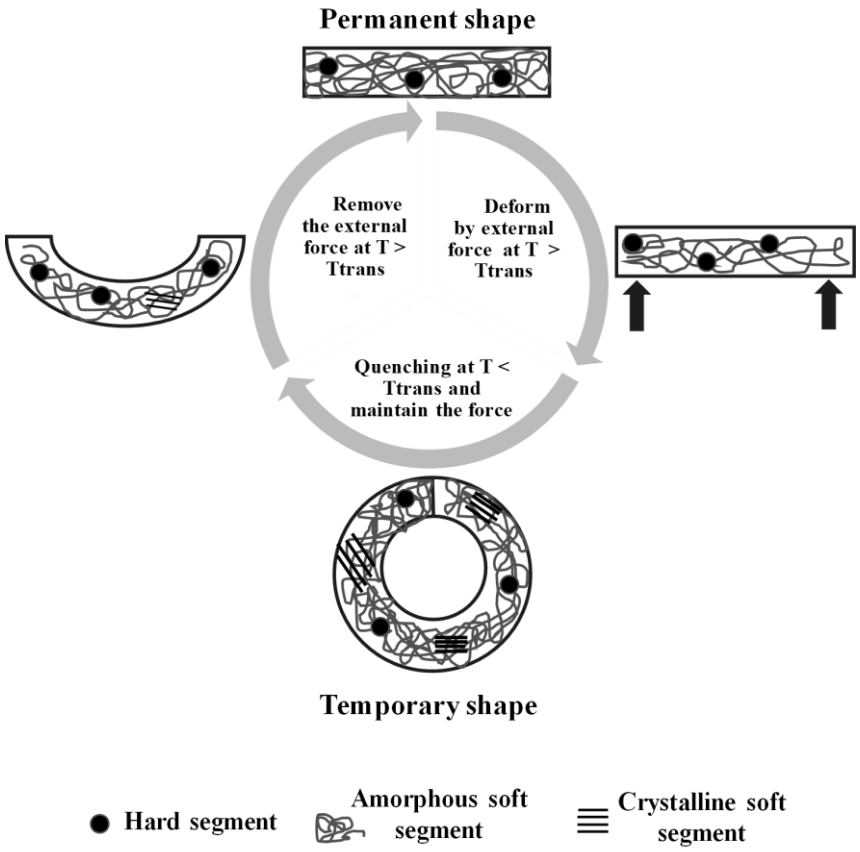

Figure 2.8: A mechanism of SME in SMPUs

2.3.2 Preparation of SMPUs

2.3.2(a) Materials

A phase-segregated block SMPU copolymer is included three basic raw materials, which are (i) Diisocyanate, (ii) Long chain polyols or macro-glycols, and (iii) Chain extender. The hard segments are produced from diisocyanate and chain extender while the soft segments are formed from macro-glycols. The urethane linkage (─NHCOO─) is formed by a reorganization reaction of a diisocyanate (-NCO) and a macro-glycol (-OH) (Hu, 2007). A typical synthesis of segmented SMPU is shown as Figure 2.9.

The structure of diisocyanate can be aromatic, aliphatic, and cycloaliphatic. The structure of diisocyanate influences greatly to the properties of SMPU; therefore, SMPU is synthesized with different types of diisocyanate, even though under same condition, resulting different mechanical characteristics (Huang et al., 2012). The common di-isocyanates that have been used to produce SMPU are 4,4-diphenyl methane diisocyanate (MDI), iso-phorone diisocyanate (IPDI), toluene diisocyanate (TDI), polymeric methylene diphenyl diisocyanate (PMDI), lysine diisocyanate (LDI) (Thakur and Hu, 2017), and 4,4'-Methylenebis (Cyclohexyl isocyanate) (HMDI) is also a potential candidate in fabrication of SMPUs (Firdaus et al., 2015).

MDI and TDI are widely used in the synthesis of SMPU because aromatic di-isocyanates possess advantages over aliphatic one such as higher reactive ability, synthesized SMPUs perform good thermal and mechanical behaviors. However, SMPUs synthesized from aliphatic di-isocyanates exhibit good oxidation and hydrolysis resistance, ultraviolet stabilization, and impact value compared with the one

obtained from aromatic di-isocyanates (Chattopadhyay and Raju, 2007, Firdaus et al., 2015, Corcuera et al., 2010)

Macro-glycols with the molecular weights that are mainly in range of 400-5000 g/mol, are used to synthesize SMPUs (Petrović et al., 2017). SMPU will be soft and flexible if the long chain polyols containing low functionality are used while a brittle and stiff SMPU is obtained when using the short-chain polyols. Polyester and polyether polyols are typically used to synthesize SMPU (Hu, 2007). Polyester polyols distribute high flexibility while polyether polyols provide some characteristics such as crystallinity, hydrophilicity, and so on. Normally, poly(ε-caprolactone) (PCL) and polyethylene glycol (PEG) have been used to synthesize SMPUs with crystalline switching segments (Hu, 2013).

Chain extender plays an important role in increasing the length of molecular chain and the molecular mass of SMPUs as well. The hard segments that made from diisocyanate and chain extender play a role as filler particles and physical crosslinking to help increase mechanical strength. 1,4-butanediol (1,4-BDO), 1,6-hexanediol, ethylene glycol, 4,4′-dihydroxy biphenyl (DHBP), and ethylene diamine are often used in producing of SMPU (Leng and Du, 2010).

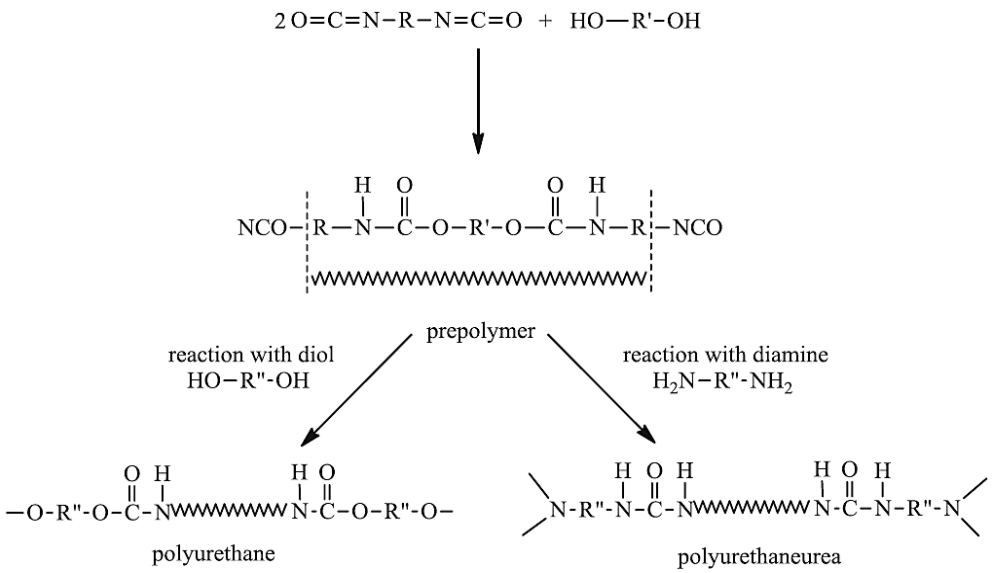

Figure 2.9: A typical synthesis of segmented SMPU by two-step pre-polymerization (Zain and Zubir, 2016)

2.3.2(b) Polymerization process

SMPUs are generally synthesized by the similar technique of traditional polyurethane, a two – step prepolymer method that can be in solution or in bulk (Mahapatra et al., 2014, Erden and Jana, 2013, Kim et al., 1996). The overall procedure is revealed in Figure 2.10. In the first step, pre-polymerization, a polyol reacts with an excess diisocyanate to form isocyanate-terminated prepolymers. In the second step, a chain extender is added to complete polymerization and a phase separated SMPU copolymer are obtained.

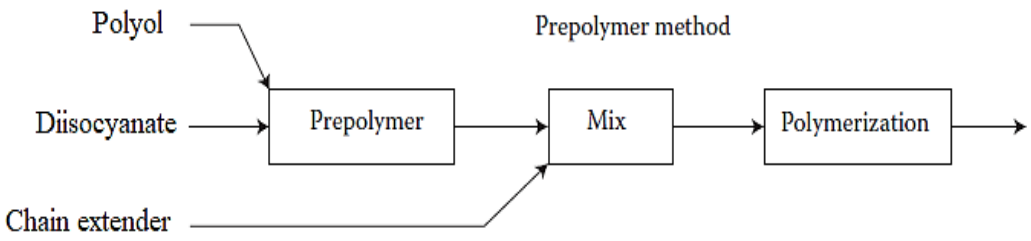

Figure 2.10: The overall process of two-step pre-polymer (Szycher, 2012)