PREPARATION AND CHARACTERIZATION OF SELF-HEALING POLYURETHANE

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PREPARATION AND CHARACTERIZATION OF SELF-HEALING POLYURETHANE

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Preparation and Characterization of Self-Healing Polyurethane". I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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Date: 19/8/2022

Witness by

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Date: 19/8/2022

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LIST OF SYMBOLS

°C   Degree Celsius

%   Percentage

T_g Glass transition temperature

η Self-healing efficiency

MPa   Mega Pascal

cm   Centimeter

LIST OF ABBREVIATIONS

DMG	Dimethylglyoxime
DBTDL	Dibutyltin dilaurate
DSC	Differential Scanning Calorimeter
FTIR	Fourier-Transform Infrared Spectroscopy
IPDI	Isophorone diisocyanate
PKOp	Palm kernel oil polyol
PTMEG	Polytetramethylene ether glycol
PU	Polyurethane
PUI	Polyurethane ionomers
SHP	Self-healing polymer
SHPU	Self-healing polyurethane
WBPU	Waterborne Polyurethane
-OH	Hydrogen bonding
-NCO	Isocyanate
F-CO	Free carbonyl bonding
H-CO	Hydrogen bonded carbonyl
H-NH	Hydrogen bonded amine
C-O-C	Ether group
C=C	Carbon-carbon double bond

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ABSTRAK

Poliuretana telah digunakan dalam banyak aplikasi seperti bahan binaan, automotif, marin, salutan dan pelekat, perubatan dan pembungkusan. Walau bagaimanapun, poliuretana tidak mempunyai keupayaan untuk sembuh sendiri tanpa rangsangan luar. Ini telah mengurangkan jangka hayat bahan dan meningkatkan sisa. Penyelidikan dan fabrikasi poliuretana swasembuh telah menjadi topik penting. Dalam kajian ini, poliuretana swasembuh telah disediakan menggunakan nisbah molar gliserol yang berbeza untuk memanjangkan hayat bahan, mengurangkan sisa, dan meningkatkan kebolehpercayaan peranti berfungsi. Matlamat penyelidikan ini adalah untuk menghasilkan poliuretana swasembuh (SHPU) dengan pelbagai kandungan gliserol melalui kaedah prapolimer dan untuk menyiasat kesan pelbagai kandungan gliserol ke atas sifat terma, sifat tegangan dan kecekapan swasembuh poliuretana. Dibutiltin dilaurat (DBTDL) telah digunakan sebagai pemangkin, Dimethylglyoxim (DMG) sebagai pemanjang rantai, gliserol bertindak sebagai penyambung silang dan aseton sebagai pelarut. Kesan nisbah molar gliserol yang berbeza telah disiasat menggunakan spektroskopi inframerah transformasi Fourier (FTIR), calorimeter imbasan pembeza (DSC), ujian tegangan dan ujian swasembuh. Berdasarkan keputusan yang diperolehi, ia menunjukkan bahawa penambahan gliserol dalam SHPU meningkatkan pemanjangan pada takat putus dan kecekapan swasembuh sambil mengurangkan kekuatan tegangan dan modulus keanjalan SHPU.

PREPARATION AND CHARACTERIZATION OF SELF-HEALING POLYURETHANE

ABSTRACT

Polyurethanes have been used in many applications such as building materials, automotive, marine, coating and adhesive, medical and packaging. However, polyurethanes do not have the ability to self-heal without external stimuli. This has reduced the lifetime of material and increase the waste. The research and fabrication of self-healing polyurethane has become important topic. In this study, self-healing polyurethane was prepared using different molar ratio of glycerol to extend the lifetime of material, decrease waste, and boost the dependability of functional devices. The aim of this research is to fabricate self-healing polyurethane (SHPU) with various content of glycerol via prepolymer method and to investigate the effect of various content of glycerol on thermal properties, tensile properties and self-healing efficiency of polyurethane. The self-healing polyurethane was prepared via two-step bulk polymerization process incorporated with Polytetramethylene ether glycol (PTMEG) and palm kernel oil (PKOp) as soft segment, Isophorone diisocyanate (IPDI) as hard segment, Dibutyltin dilaurate (DBTDL) as catalyst, Dimethylglyoxime (DMG) as chain extender, glycerol acted as crosslinker and acetone as solvent. The effect of different molar ratio of glycerol was investigated using Fourier-transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC), tensile test and self-healing test. Based on the results obtained, it shows that the addition of glycerol in self-healing polyurethane (SHPU) increases the elongation at break and self-healing efficiency while decreases the tensile stress and Young's Modulus of SHPU.

CHAPTER 1

INTRODUCTION

1.1   Research Background

Self-healing polymers (SHPs) are a type of smart material that that have the ability to repair internal cracks or damage in any matrix and reconstruct the mechanical properties of the cracked section using the mechanism of autonomic healing. SHPs are used in applications such as sensors, soft robotics, 3D printing, biomaterials, textiles, and automobiles, as well as coatings or paints (Reddy, 2020).

The self-healing polymers can be classified into two categories such as intrinsic and extrinsic self-healing polymers. Intrinsic self-healing polymers are polymers that do not need an external substance to restore damage, whereas extrinsic self-healing polymers are polymers that need an external substance to restore damage. The external agent, which is often dispersed in the form of vascular systems or capsules are released to seal the damage and has no particular interaction with the matrix.

For intrinsic self-healing polymers, the process of healing is accomplished by adjusting dynamic bond interactions at the molecular level. Dynamic bonds can be divided into two groups which are covalent and non-covalent bond interactions (Hamid, 2021). The covalent bond interactions include disulfide bonds, imine bonds, Diels–Alder chemistry, transesterification reactions, ditelluride bonds, diselenide bonds, boron-based bonds and others such as alkoxyamine, oxime-urethane and urea bond as shown in Figure 1.1 (Utrera-Barrios et.al., 2020).
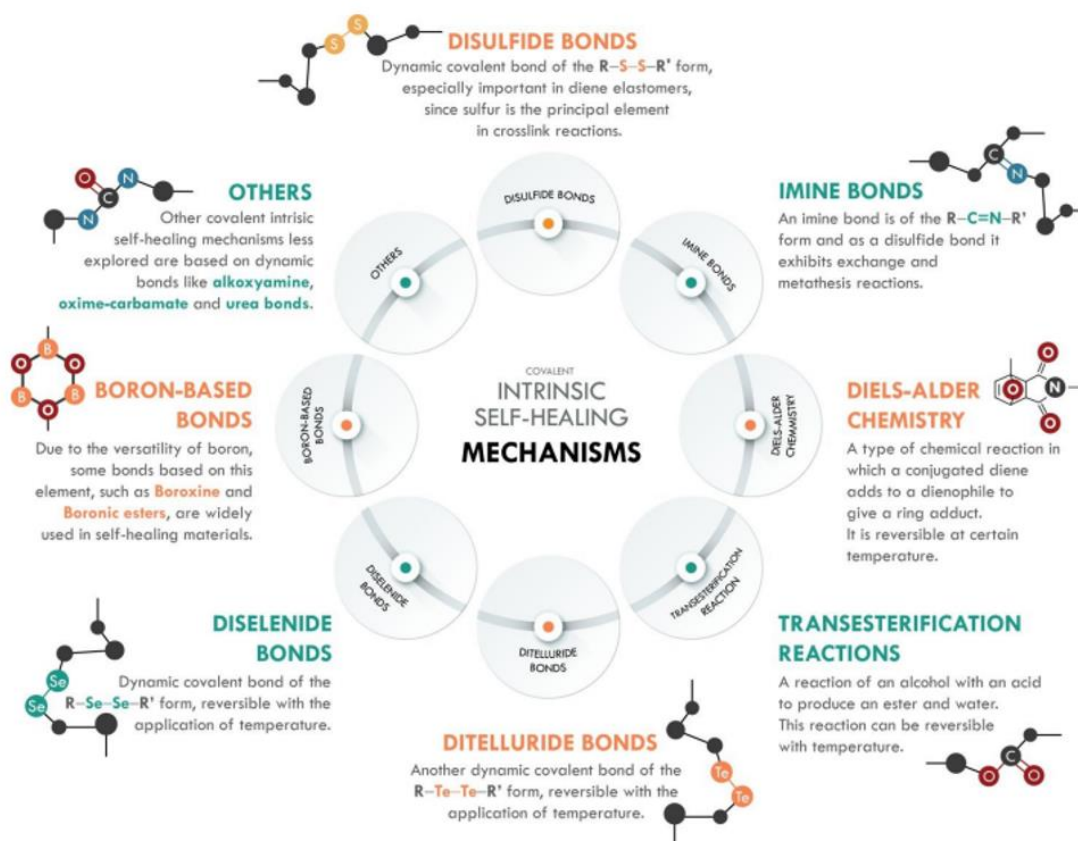
Figure 1.1: Covalent intrinsic self-healing mechanisms (Utrera-Barrios et.al., 2020).

The self-healing polymer according to disulfide bonds includes natural rubber, styrene butadiene rubber, butadiene rubber, polydimethylsiloxane and polyurethane, whereas the self-healing polymer according to Diels–Alder chemistry includes natural rubber, styrene butadiene rubber, ethylene propylene diene rubber, polydimethylsiloxane, polyurethane and styrene butadiene styrene rubber. The self-healing polymer according to imine bonds are NR latex-based elastomer and polydimethylsiloxane while the self-healing polymer according to transesterification reactions are epoxidized natural rubber and thiol-epoxy elastomer (Utrera-Barrios et.al., 2020).

The non-covalent bond interactions involve van der Waals forces, π–π stacking, hydrogen bonds, metal-ligand coordination, dipole-dipole interactions, ionic interactions,

host-guest interactions and shape memory are shown in Figure 1.2 (Utrera-Barrios et.al., 2020).
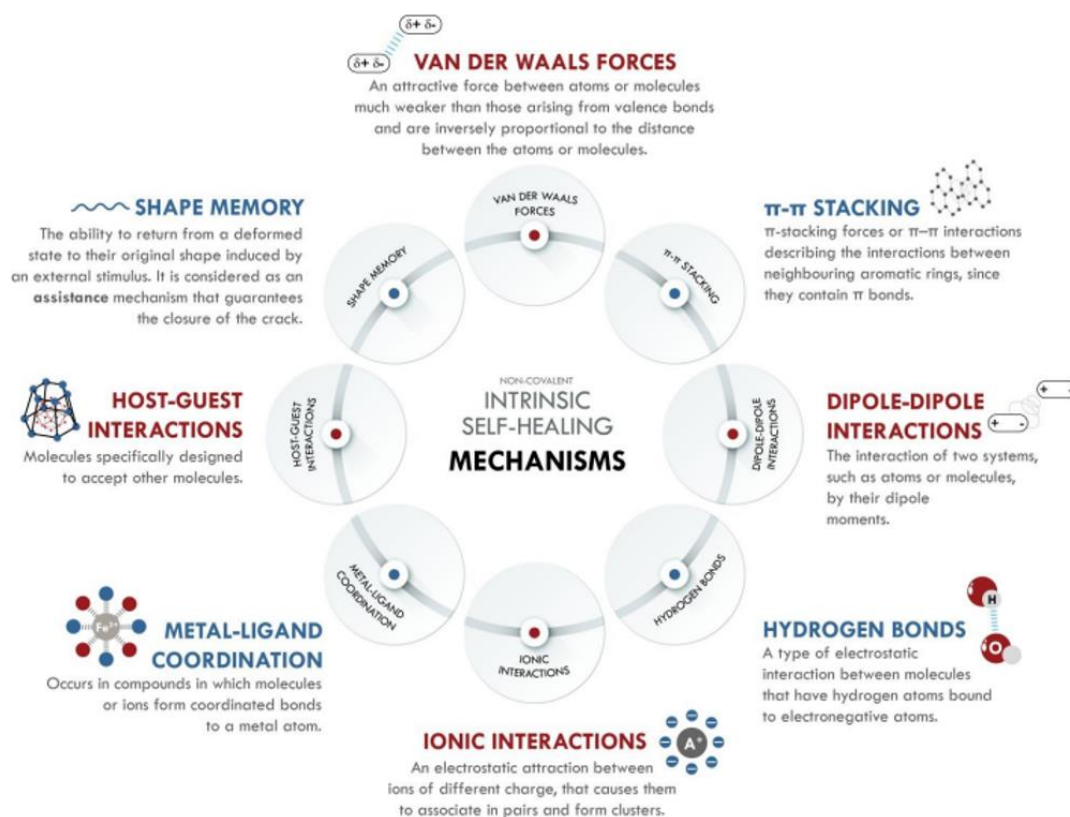
Figure 1.2: Non-covalent intrinsic self-healing mechanisms (Utrera-Barrios et.al., 2020).

The self-healing polymer attributed to dipole–dipole interactions is fluorinated elastomer while the self-healing polymer attributed to hydrogen bonding includes epoxidized natural rubber, butadiene rubber, polydimethylsiloxane, polyurea elastomer, eucommia ulmoides ester elastomer and lignin-based supramolecular elastomer. The self-healing polymer attributed to ionic interactions are natural rubber, epoxidized natural rubber, brominated natural rubber, brominated butyl rubber, ethylene propylene diene rubber, polydimethylsiloxane and polyampholytes-based elastomer, whereas the self-healing polymer attributed to metal-ligand coordination are nitrile rubber,

polydimethylsiloxane, polyurethane and aminopropyl methyl phenyl polysiloxanes. Lastly, the self-healing polymer attributed to host-guest interactions is alkyl acrylate-based elastomer (Utrera-Barrios et.al., 2020).

There are different types of polyurethane which can exhibit self-healing properties. The polyurethane according to the method of intrinsic self-healing using dynamic non-covalent bond, which are polyurethane (urea) elastomer is produced by combination of hydrogen bonds and van der Waals forces and exhibit self-healing properties. This self-healing polyurethane showed that the fundamental builder for the material to self-heal are the cross-linking of the hydrogen bonds and van der Waals forces, and temperature was the main determinant which influence these forces. Besides that, Cu(II)-dimethylglyoxime-urethane-complex-based polyurethane elastomer (Cu-DOU-CPU) also exhibit self-healing properties. It was formed by combination of metal-ligand coordination and hydrogen bonds. Copper ions provided metal-ligand coordination, and hydrogen bonds were formed between amino groups and main chain esters. Other than that, waterborne PU (WBPU) also exhibit self-healing characteristics. It is formed by the combination of host-guest interactions as well as the formation of multiple hydrogen bonds (Utrera-Barrios et.al., 2020).

Thermoset polyurethane is polyurethane which is crosslinked using covalent bonds or in some cases, using hydrogen bonds (Katharina et.al., 2016). The cross-linking is important in thermoset polyurethane because it obstruct the molecular mobility of the chains of polymer and hence decrease the flexibility of polymer structure. As a result, crosslinking gives the polyurethane a stronger and rigid structure (Szycher, 2012).

The cross-linking is commonly introduced using trifunctional or higher-functional polyols. Furthermore, cross-links can be formed by adding extreme allophanate to the formulation and then undergo reaction with urethane groups that exist to generate

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allophanate crosslinks, or with urea group that exist to create biuret crosslinks. The cross-links form in these situations have lower heat stability than the main chains and thus open and close more often when heated. Furthermore, peroxides can cause cross-linking by either removing hydrogen or introducing vinyl groups into the polyurethane. In either case, the formed cross-links are carbon-carbon (C-C) single bonds, which have the same stability as the main chain (Szycher, 2012).

Polyols with three hydroxyl (-OH) groups, called triols, for example, glycerol, is widely used as crosslinker in thermoset polyurethane because glycerol is produced using a variety of industrial techniques that includes natural oils and fats such as triglycerides, hence it is a renewable resources (Alessandro, 1989). Besides, it is a colorless, odorless and viscous liquid that is non-toxic. Other than that, it can crosslink hard segment instead of soft segment, and cross-linking using hard segment is more efficient than that of soft segment (Chun et.al., 2007).

1.2   Problem Statements

Nowadays, self-healing polyurethane elastomer (PU) possess great potential for biomedical applications due to its self-healing feature which allows them to repair themselves after mechanical injury. However, self-healing process needs the use of external energy sources, for example, heat, light and pressure. Besides that, a lot of materials in everyday life were harmed at normal environment situations when there are no stimuli from outside present, therefore developing materials which have the capability to self-heal readily at ambient temperature is particularly desirable (Zhang et al., 2019).

Incorporating dynamic noncovalent bond interactions such as hydrogen bonds, metal-ligand coordination, host–guest interactions, ionic interactions, dipole-dipole interactions and van der Waals forces, and dynamic covalent bond interactions such as

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disulfide bonds, imine bonds, boron-based bonds are typical technique for designing materials that self-heal at ambient temperature (Si et.al., 2020).

Although a little quantity of noncovalent bond interactions can result in excellence self-healing, the materials produced are very weak. On the other hand, a huge amount of noncovalent bond interactions may enhance mechanical properties, but self-healing, stretchability, and toughness of materials will degrade. Aside from that, these types of materials have narrow resilience and tend to creep because of their linear molecular structures. The structures that cross-linked according to dynamic covalent bonds including urea bonds, boron-oxygen bonds and disulfide bonds can produce materials which are strong and healable. However, the networks of crosslinking limit the mobility of chains and decrease the capability of self-healing (Zhang et al., 2019).

Hence, a new technique was introduced by using dimethylglyoxime-urethane-based polyurethane elastomer which generates a polyurethane elastomer that are covalently cross-linked according to dynamic oxime-urethane bonds instead of cross-linked polyurethane elastomer based on dynamic noncovalent bond interactions and dynamic covalent bonds owing to their potential to simultaneously enhance the mechanical characteristics and the self-healing ability of materials (Zhang et al., 2019).

1.3   Research Objectives

The objectives in this project are:

1. To fabricate self-healing polyurethane with various content of glycerol via prepolymer method.

2. To investigate the effect of various content of glycerol on thermal properties, tensile properties and self-healing efficiency of polyurethane.

1.4   Research Approach

For this project, self-healing polyurethanes were prepared using prepolymer method, with different molar ratio of glycerol to study the effect of varying different amount of glycerol on the properties of polyurethane. There are various characterization techniques were used to investigate the thermal properties, tensile properties and self-healing efficiency of polyurethane such as Fourier-transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC), tensile test and self-healing test.

Firstly, PTMEG and PKOp are dried overnight in a vacuum oven at 80°C prior to synthesis. In the first step, PTMEG was premixed with IPDI and a drop of DBTDL in a three-neck round bottom flask under continuous stream of nitrogen gas at 50°C using a hot plate for 3 hours. Meanwhile, the mixture was stirred using magnetic stirrer in the flask which is still kept in silicon oil bath and equipped with a thermometer. After 3 hours, PKOp was injected slowly to the mixture and the reaction was carried out for another 2 hours. After 2 hours, the obtained prepolymer was reacted with acetone, DMG and glycerol at room temperature for 1 hour. Lastly, the PU sample was then poured into polytetrafluoroethylene mould and put into vacuum oven for 48 hours.

The PU sample was then analysed using FTIR to analyze the functional groups and composition. DSC was performed to determine the thermal properties of the sample whereas tensile test was carried out to determine the tensile properties of the sample. Lastly, self-healing test was carried out to determine the self-healing efficiency of the sample.

1.5   Thesis Outline

This thesis involves 5 chapters.

Chapter 1 covers the introduction part of overall project which involving the research background, problem statements, research objectives and research approach.

Chapter 2 covers the literature review on the polyurethane, raw materials used for polyurethane such as polyol, isocyanate, catalyst, chain extender, crosslinker and other additives, preparation method for polyurethane, type of polyurethane, mechanism of self-healing polyurethane, factors that affect the properties of SHPU, type of SHPUs through dynamic covalent chemistry and type of SHPUs through supermolecular chemistry and applications of oxime-urethane based polyurethane.

Chapter 3 describes the raw materials, experimental method which include synthesis of self-healing polyurethane and sample preparation, and characterization method used in this project.

Chapter 4 presents the results and discussion of the research.

Chapter 5 summarizes the overall conclusion of the project which including the recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Polyurethane

Polyurethane (PU) is a polymer that has the urethane (-NH-CO-O-) group. The urethane group is normally formed by react isocyanate (NCO) groups and hydroxyl (-OH) groups (Rahman et al. 2019). The chemical structure of urethane group is shown in Figure 2.1.
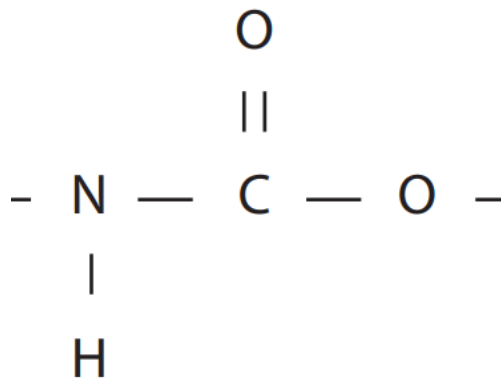
Figure 2.1: The chemical structure of urethane group (Szycher, 2012).

Polyurethane could be divided into some categories which are flexible and rigid foam, thermoplastic and thermoset, waterborne, coating, sealants, adhesives, elastomers and binders. The flexible and rigid foams are utilised in various industries. PU foams can be adjusted to attain specified qualities by replacing the type and quantity of polyols, isocyanates, catalysts, surfactants and blowing agents used in their preparation. Besides, PU are commonly employed in coatings and adhesives because it offers outstanding mechanical strength, superior resistant to abrasion, corrosion, and chemical, as well as flexible at low temperature. Elastomer is another important category of PU, which can be easily incorporated into different engineered products. PU elastomers are considered as flexible polymers that can be treated by using injection moulding and extrusion and have a great potential to be recycle (Rahman et al., 2019).

Polyurethane is typically prepared by react isocyanate and polyol molecules in combination with either ultraviolet light activation or a catalyst. These polyol molecules and isocyanate must contain two or more hydroxyl groups and isocyanate groups respectively (Akindoyo et al., 2016). Polyurethane can be fabricated using various monomers of isocyanates, polyols and chain extenders. The characteristics of polyurethane also vary depending on the contents of polyols, diisocyanate and chain extenders used (Rahman et al., 2019). The synthesis of polyurethane is shown in Figure 2.2.
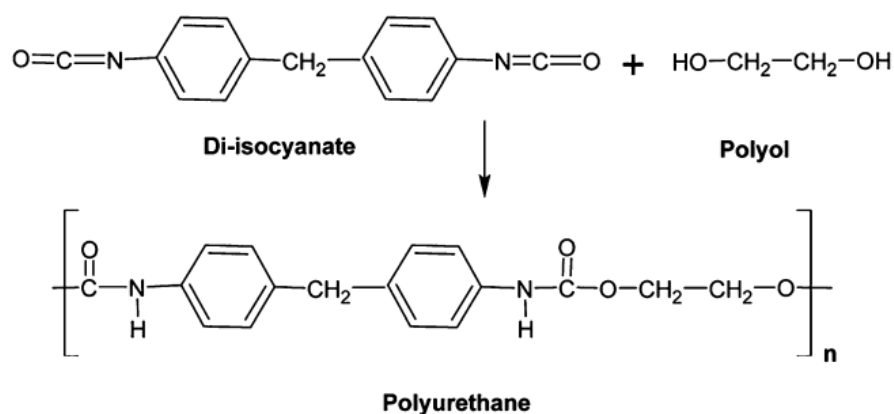
Figure 2.2: Synthesis of polyurethane (Rahman et al., 2019).

Isocyanate, polyol, catalyst, chain extender and crosslinker are generally used for the synthesis of polyurethane. Isocyanates, with the functional group (R-NCO) are very reactive and toxic materials. It consists of monoisocyanate, diisocyanate, polyisocyanate, aliphatic isocyanate and aromatic isocyanate. Polyol is a type of alcohol which consists of more than one hydroxyl group (R-OH) per molecule and can be categorized into polyether polyol (-ROR) and polyester polyol (-OCOR). Polyether polyol is created by ring-opening polymerization of epoxy monomers, whereas polyester polyol is created by polycondensation of carboxylic acid and hydroxyl groups (Rahman et al., 2019).

Isocyanate (hard segment) is used to control the rigid and tough properties, whereas polyol (soft segment) is used to maintain the elastomeric properties. Excess

isocyanate or an external crosslinker can be used to create PU which is cross-linked with improved mechanical characteristics. On the other hand, excess crosslinker in the structure of PU will decrease the mechanical characteristics. As a result, hard and soft segments combined with moderate amount of cross-linking can yield PU foam with improved mechanical properties (Rahman et al., 2019).

During the synthesis of polyurethane, the utilization of suitable amount of catalyst was also crucial. This is due to a little quantity of catalyst enables the isocyanate and polyol to react quickly. The most frequently used catalysts in synthesis of PU are dibutyltin dilaurate, dibutyltin dilauryl mercaptide and dibutyltin diacetate which act as organometallic catalyst (Rahman et al., 2019).

Preparation of PU by using renewable sources, for example, vegetable oil-based materials as polyols have been drawn attention because it is commercial and environmental friendly. Vegetable oils are primarily composed of triglyceride molecules, which have a variety of reactive sites, including carbon-carbon (C=C) double bonds, hydroxyl (O-H) groups and ester (R-C=O-R') groups. These oils can be converted to polyols using a variety of processes, including ozonolysis, hydroformylation epoxidation and ring-opening polymerization, and transesterication. Palm kernel oil can be used to replaced part of polyol (soft segment), which will lead to different properties (Akindoyo et al., 2016).

2.1.1 Raw materials

2.1.1(a) Polyol

Polyol, also known as soft segment, consists of two or more hydroxyl (–OH) groups in each molecule. Polyol with low molecular weight is used to control the rigidity of polyurethane, whereas polyol with high molecular weight promote elastomeric characteristics of polymeric materials (Rahman et al., 2019).

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There are two commonly used polyols which are polyether polyols or polyester polyols. Polyether polyol is created by ring-opening polymerization of epoxy monomers, whereas polyester polyol is created by polycondensation of carboxylic acid and hydroxyl groups. Tetrahydrofuran can be polymerized to create polytetramethylene ether glycols (PTMEG), a typical form of polyether polyol that is mostly employed in very effective elastomeric applications (Rahman et al., 2019). Example of polyether polyols and polyester polyols which commonly used are shown in Figure 2.3 and Figure 2.4.
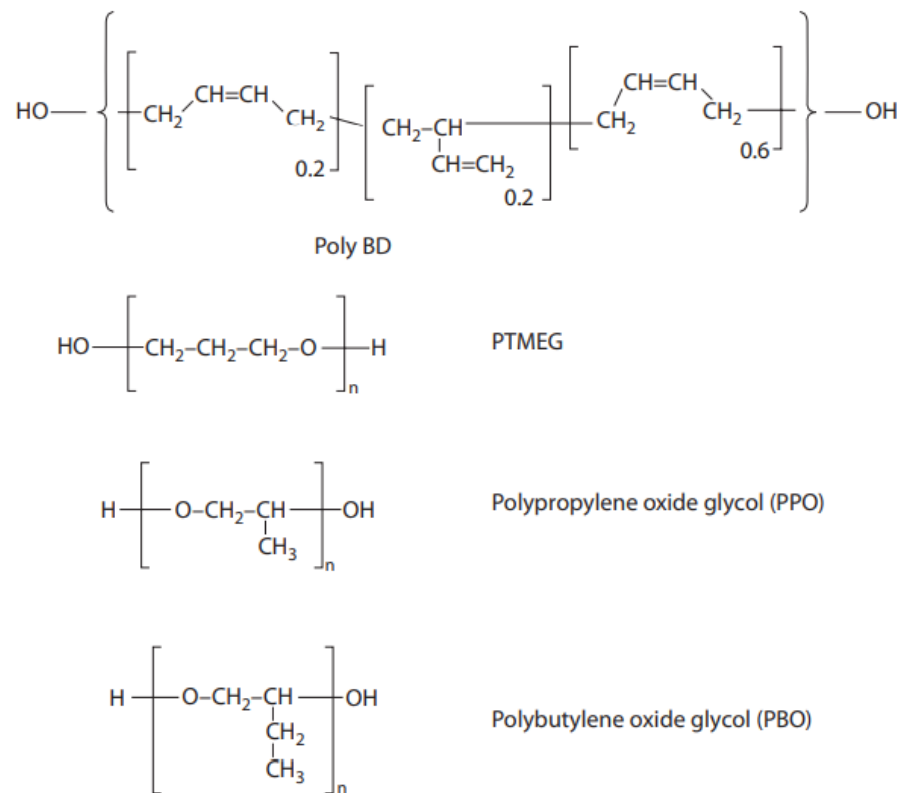
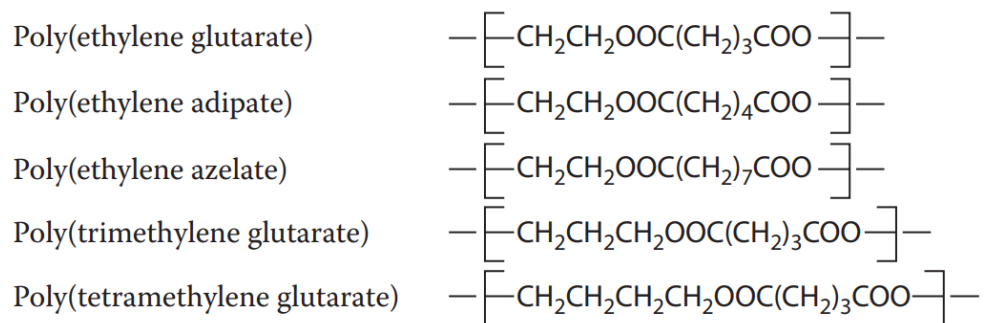Figure 2.3: Example of polyether polyols and their structure (Szycher, 2012).

Figure 2.4: Example of polyester polyols and their structure (Szycher, 2012).

Polytetramethylene ether glycols (PTMEG) is widely used polyol in synthesis of polyurethane due to its good comprehensive properties such as excellent hydrolytic stability, excellent flexibility and impact resistance, and premium pricing to prepare high performance polyurethane. Polyurethane products made from PTMEG have excellent low-temperature characteristics, high engineering toughness, resilience, and inherent hydrolysis resistance (Szycher, 2012).
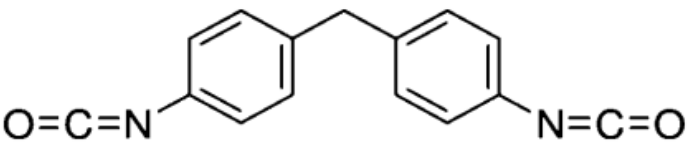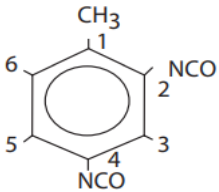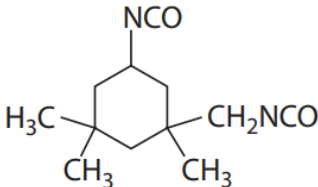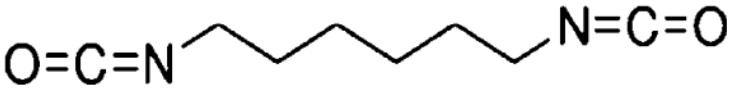
2.1.1(b) Isocyanate

Isocyanate is a family of highly reactive, low molecular weight chemicals and consists of (R-NCO) functional group. It is also known as hard segment and is used for reactivity and curing properties. Diisocyanates, which contain two isocyanate groups, either aliphatic or aromatic are mainly utilised in polyurethane and their by-products (Rahman et al., 2019). The examples of widely used aromatic isocyanates are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate whereas example of widely used aliphatic isocyanates used are hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI) (Souza et al., 2021).

Aromatic isocyanates add rigidity to the structures and influence the general characteristics of polyurethanes. Hence, they are used in applications of rigid and thermoset polyurethanes. PU according to aromatic isocyanate possess greater mechanical properties. Besides, they are usually cheaper and more reactive compared to other type of diisocyanates, thus they are recommended isocyanates for use in industry. However, PU material using aromatic isocyanates will yellowing with time. Aliphatic isocyanates are utilised frequently in coatings as they can combine with pigments perfectly, maintain gloss aspect, and stabilised towards ultraviolet light (Rahman et al., 2019).

Aromatic isocyanates are typically used to create flexible foams, such as slabstock foam used to make mattresses or the moulded foam used in automotive seats. In addition, they can be utilised to produce rigid foams such as insulation for refrigerators and make elastomers. Aliphatic isocyanates are employed in coatings applications and other situations where colour and transparency are particularly required (Rahman et al., 2019). The example of widely used diisocyanates and their structure are shown in Table 2.1.

Table 2.1: Example of widely used isocyanates and their structure (Rahman et al., 2019).

Isocyanate	Structure
4,4'-Methylenebis(phenyl isocyanate), MDI	
Toluene 2,4-diisocyanate, TDI	
Isophorone diisocyanate, IPDI	
Hexamethylene diisocyanate, HDI	

MDI is the least dangerous isocyanates among the commonly used isocyanates; but it is still poisonous. It has a lower vapor pressure, which decrease the risks when handling when in comparison with the other frequently used isocyanates, such as TDI and HDI. TDI is a poisonous and extremely reactive chemical that undergo reaction with water violently and exothermically, producing carbamic acid that is not stable and hence

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it decomposes to form a primary amine and emits CO_2. The toxic effects of TDI could be related to two potential toxic actions which are primary irritating action on the mucous membranes of the ocular, gastrointestinal and respiratory tracts, as well as bronchospasm because of an immunological or pharmacological reaction (Kapp, 2014).

HDI is an industrial compound that is not found in nature. It is a highly reactive and combustible synthetic organic chemical. The possible hazards of this substance are linked to the manufacture, dealing, consumption, and discarding of HDI and goods or materials consists of HDI. HDI is a severe respiratory sensitizer that can also irritate the eyes, nose, throat, and lungs. IPDI is typically employed in the chemical synthesis of aliphatic polyisocyanates and polyurethanes due to the nondiscoloring property of IPDI and the isocyanates in the IPDI have relative higher steric effect than other isocyanates such as HDI and HMDI, hence IPDI was commonly used in the synthesis of polyurethane (Kapp, 2014).

2.1.1(c) Catalyst

Catalyst is used to accelerate the polyol and isocyanate reaction. Catalysts that are frequently used in PUs are classified into two types which are metal complexes and amine compounds. Metal complexes are made up of bismuth, zinc, lead, mercury and tin compounds such as dibutyltin dilaurate (DBTDL) and dibutyltin diacetate. Tertiary amines have traditionally been used as amine catalysts, such as dimethylethanolamine (DMEA), dimethylcyclohexylamine (DMCHA), 1,4-diazabicyclo[2.2.2]octane (DABCO) and triethylenediamine (TEDA) (Rahman et al., 2019). The widely used catalysts in PU synthesis are illustrated in Figure 2.5. Dibutyltin dilaurate (DBTDL) is an organotin compound which commonly used as a catalyst for production of polyurethane from isocyanates and polyols because it is very efficient, hence a very low level of catalyst will greatly increase the NCO/OH reaction rate.
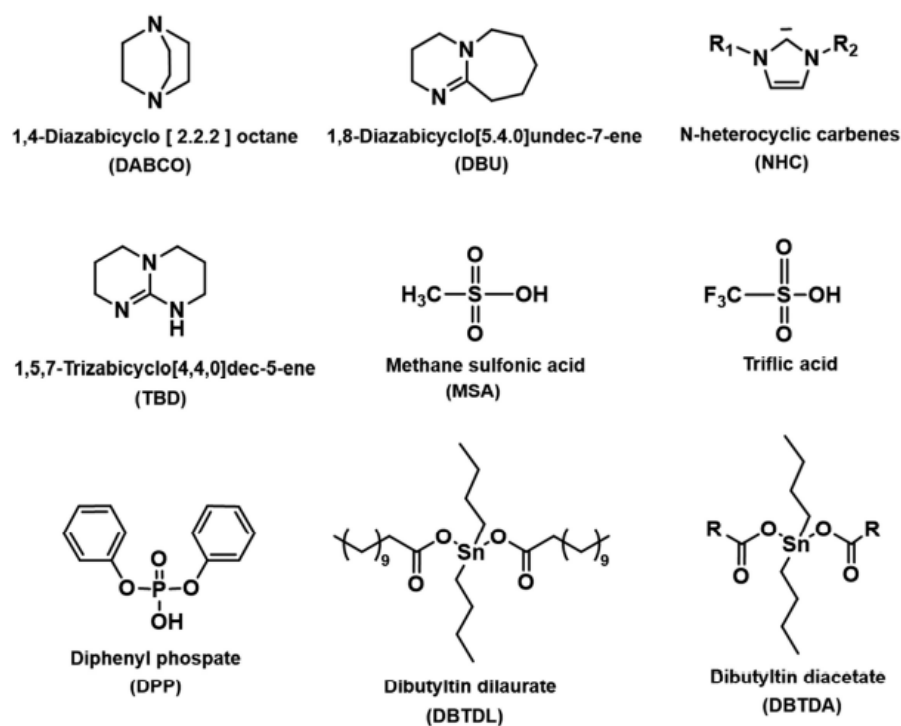
Figure 2.5: Example of widely used catalyst in PU synthesis (Souza et al., 2021).
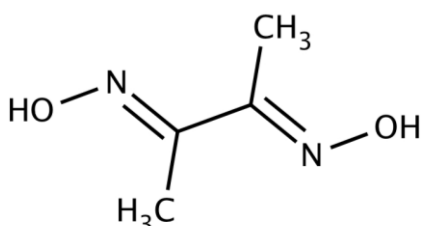
2.1.1(d) Chain extender

Chain extender is low molecular weight diol or diamine and is usually hydroxyl- or amine-terminated compounds that have a functionality of 2 and is used to add stiff domains in the structure of polymer. Chain extender could influence shape, cellular structure, thermal and mechanical characteristics of the PU, therefore proper selection is needed. PU will have reduced mechanical strength if there is very little chain extender; the mechanical strength is improved with more chain extender. Even so. PU will become fragile using a very high quantity of chain extender (Rahman et al., 2019).

Chain extender made from diol produce a urethane linkage. The examples of diol chain extender including butane diol, ethylene glycol, and propylene glycol. Chain extender made from diamine such as putrescine, ethylene diamine, and diaminopropane produce a urea linkage that leads to bidentate hydrogen bonding. Diamine chain extender

has a higher modulus and tensile strength but lower elongation in comparison with their diol counterparts (Touchet et al., 2016). Table 2.2 listed some examples of frequently used chain extender in polyurethanes and their chemical structure.

Table 2.2: Some examples of frequently used chain extender used in polyurethanes and their chemical structure (Akindoyo et al., 2016).

Chemical name	Structure
1, 4-Butane diol	$HO–CH_2CH_2CH_2CH_2–OH$
Ethylene diamine (ED)	$H_2N–CH_2CH_2–NH_2$
Trimethylol propane	$CH_2–O–CH_2CH_2–OH$ | $H_2C–CH_2–C–CH_2–CH_2–OH$ | $CH_2–O–CH_2CH_2–OH$
Dimethylglyoxime (DMG)	

Dimethylglyoxime (DMG) is mostly used chain extender in synthesis of polyurethane because of its adjacent oxime groups, which facilitate the reverse motion of the polymer chain (Liu et.al., 2019).

2.1.1(e) Crosslinker

Crosslinker is additive of low molecular weight and is usually hydroxyl- or amine-terminated compound that has a higher functionality which produce a covalent bonding between the chains of polymer and results in a tightly interconnected network.

Hence, it is employed to alter structures in order to enhance their mechanical and barrier qualities (Akindoyo et al., 2016).

Polyisocyanate hardener, melamine, and trifunctional or higher-functional polyols such as glycerol are usually used as a crosslinker. The amount of crosslinker used need to be suitable because excess crosslinker will has detrimental effect on properties (Rahman et al., 2019). Glycerol is widely used chemical crosslinker in synthesis of polyurethane because it is non-toxic, natural resources and consists of three hydroxyl groups which can crosslink hard segment instead of soft segment, and cross-linking using hard segment is more efficient than that of soft segment (Chun et.al., 2007).

2.1.1(f) Other additives

Other additives that are added consists of surfactants and blowing agents. Surfactants are elements that are introduced throughout the polyurethane production process to ensure correct stirring between the polyol and isocyanate group. Surfactants are used to give the consistency in growing cellular structures. The majority of surfactants are silicon-based block polymers, for example, polydimethylsiloxane-polyoxyalkylene, or silicon oils like nonylphenol ethoxylates (Souza et al., 2021).

Blowing agents are chemicals which added to polyurethanes throughout the process of formulation to generate foam by lowering density and enlarging porosity. They could be classified into two categories which are physical and chemical blowing agents. Physical blowing agents are gases that are blown directly into the mixture of polyurethane throughout the process of foaming. The examples of physical blowing agents including chlorofluorocarbons (CFCs) such as trichlorofluoromethane and dichlorodifluoromethane. Chemical blowing agents are chemicals that decompose chemically, resulting in the generation of gases that create the blowing effect. Water is

the most basic and widely utilised chemical blowing agent, which is highly reactive when react with isocyanate, hence results in the generation of CO_2 (Souza et al., 2021).

2.1.2 Preparation method for polyurethane

2.1.2.1 One-step process

Figure 2.6 shows the polymerization of polyurethane based on one-shot method where all components such as isocyanate, polyol and chain extender are combine using one step to produce polyurethane (Touchet et al., 2016). It is the most straightforward, quickest, and most cost-effective manufacturing technology, and it is frequently used in highly competitive commodity areas like flexible foam. However, it is more difficult to control the properties of the polyurethane (Szycher, 2012).
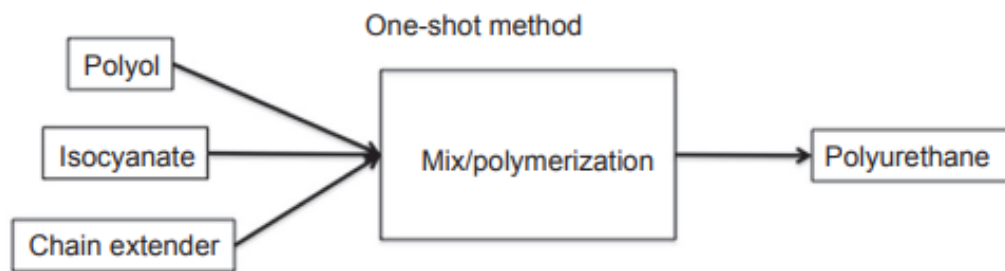
Figure 2.6: The polymerization of polyurethane based on one-shot method (Touchet et al., 2016).

2.1.2.2 Two-step process

Figure 2.7 shows the polymerization of polyurethane based on the prepolymer method. The polyols were first premixed with isocyanate to form prepolymer. In the second stage, the prepolymer is undergo reaction with a chain extender to increase molecular weight and produce a straight block copolymer with varying blocks of hard segment and soft segment. This strategy results in a more organised structure and greater property control (Touchet et al., 2016).
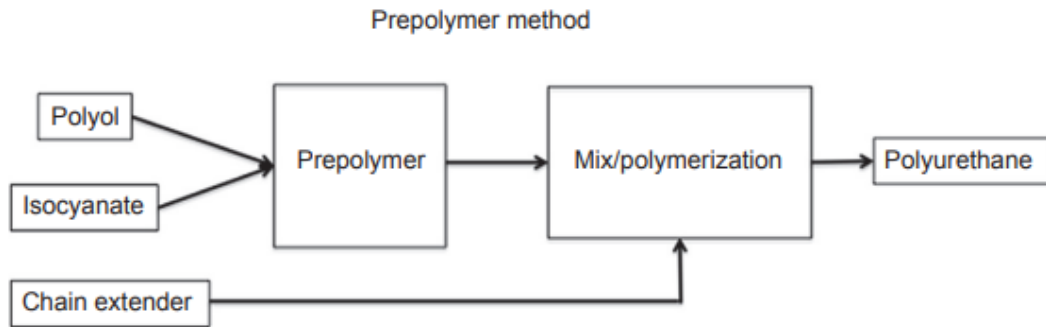
Figure 2.7: The polymerization of polyurethane based on the prepolymer method (Touchet et al., 2016).

2.1.3 Types of polyurethane

2.1.3.1 Thermoplastic polyurethane

Thermoplastic polyurethane is a straight segmented block copolymer, made up of hard and soft segments that may bend plastically when heated and solidify again when cooled. It can be manufactured using a various method such as solution coating and vacuum forming, as well as extrusion, blow, compression, and injection moulding equipment. They are elastic and flexible, and are resistant to weather and abrasion. The combinations of several property for thermoplastic polyurethanes makes them suitable to be used in many applications, including those in the construction, automotive, and footwear industries (Akindoyo et al., 2016).

2.1.3.2 Thermoset polyurethane

Thermoset polyurethane is a crosslinked network that possess strong mechanical properties and resistant to solvent and is employed in durable goods, adhesives, and composites. They cannot be melted and reformed once they have been fully cured. They are frequently employed as manufactured goods due to their physical attributes and processing simplicity (Aristri et al., 2021).

There are several types of thermoset polyurethane, including soft foam and hard foam. Soft foams are employed to make quilts, furniture, and packaging fabrics, whereas hard foams are utilised in make materials for thermal insulation. They are very ductile and have a rubbery resin with high strength and a low glass transition temperature. They are also having good workability if processed using the same machinery and operating conditions as thermoplastic polyurethanes (Ali, 2017).

The raw materials commonly used in synthesis of thermoset polyurethane are polyol, isocyanate and crosslinker. Vegetable oil is also one of the required raw materials as it is primarily made up of triglycerides. It is an ester from glycerol and fatty acids, which are mainly saturated and unsaturated compounds. Figure 2.8 shows the general pathway for synthesis of thermoset polyurethane.
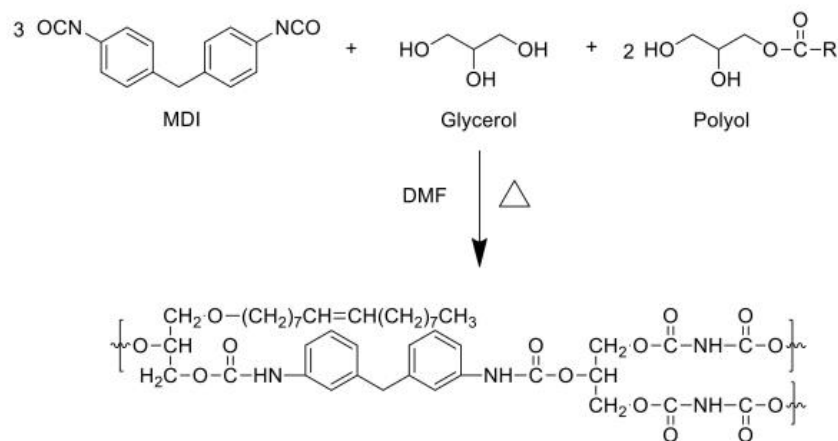
Figure 2.8: General pathway for synthesis of thermoset polyurethane (Szycher, 2012).

2.1.3.3 Polyurethane foams

PU foams come in 2 different varieties, including rigid and flexible foams. Rigid PU foams can be made by combining bio-based polyols generated from plant lignin or vegetable oils with petroleum-based polyols. The applications for the rigid PU foams include insulation and flame retardant. Blowing and gelling are two major steps in the

synthesis of flexible PU foams. Urea and carbon dioxide are generated during the reaction of blowing, which causes them to enlarge and be entangled by the reaction mixture, whereas urethane linkages are generated when the isocyanate and hydroxyl group of the polyol are reacted. Flexible PU foams are mostly used in packaging, cushioning, bedding furniture, carpet underlays, biomedicine, vehicle interiors, and nanocomposites (Akindoyo et al., 2016).

2.1.3.4 Polyurethane ionomers (PUI)

Polyurethane ionomers are polyurethanes that have ionic groups in the polyurethane backbone chain. They have a variety of benefits, including improved dispersion in polar solvents and improved thermal and mechanical properties due to their increased hydrophobicity. PUI can be made by incorporating ionic groups via diisocyanate-containing ionic groups or ionic diols. The shape memory effect of PUI makes it a particularly valuable material for biomedical equipment such as connection tubing for heart pacemakers and artificial hearts (Akindoyo et al., 2016).

2.1.3.5 Coatings, Adhesives, Sealants, and Elastomers

Coatings, adhesives, liners, and elastomers are some of the most promising applications for PU and its by-products because of its superior mechanical, thermal, chemical, and physical characteristics. A PU must have sufficient scratch resistance, high chemical resistance, low temperature flexibility, excellent drying, and acceptable adhesive qualities in order to be used in coating applications. (Rahman et al., 2019).

PU adhesives are good at bonding, while PU sealants can produce extremely tight seals. Elastomers refer to the rubber-like properties of a polymer, where it able to return its original shape when a load is removed from the material. Hence, elastomers can be used in applications such as footwear, ski boots, eyewear, home goods, and automobile components (Akindoyo et al., 2016).

2.1.3.6 Binders

Polyurethane binders are frequently used to combine different types of fibres and other materials. PU binder can create a long-term glueing effect between long-strand lumber, laminated veneer lumber, organic materials, oriented strand boards, medium density fibre boards, particle boards, and straw boards. PUs requires outstanding heat stability and a high ratio of hard or soft segments when it is utilised as a binding material. A suitable binder also needs to have a particular or moderate acid number, a small molecular weight, weak crystallinity, and a restricted particle distribution if PU dispersion. They are employed in processes like ink-jet printing, the fabrication of wood panels, the foundry industry, and the manufacture of rubbery or elastomeric flooring surfaces (Akindoyo et al., 2016).

2.1.3.7 Waterborne Polyurethane (WBPU) Dispersions

Waterborne Polyurethane (WBPU) is a colloidal system with two different segments, in which the particle of polyurethane is dispersed in water. They are mostly prepared by using water as main solvent. WBPU provides various benefits, including low viscosity, environmentally friendly, cheaper, and ease of application. There are some examples of waterborne polyurethanes such as coatings, adhesives, sealants and binders. The varieties and quantities of polyol, isocyanate, ionomers, and chain extender used are contributed to diverse properties of this dispersion (Rahman et al., 2019).

2.2 Mechanism of self-healing polyurethane (SHPU)

2.2.1 Extrinsic self-healing

The healing agent is encapsulated into the polymer matrix after it has been pre-embedded in the microcapsules or microvascular. When the materials are destroyed, capillary forces can transport the healing agent to the damage zone and heal the materials.

These types of the materials have limited healing times because of the exhaustion of the healing agent (Fu et al., 2018). Figure 2.9 shows the mechanism of intrinsic self-healing.
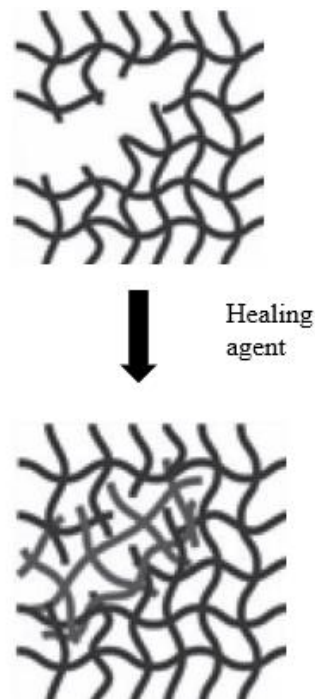

Figure 2.9: Mechanism of extrinsic self-healing (Billet et.al., 2012)

2.2.2 Intrinsic self-healing

Intrinsic self-healing materials are materials in which the polymer structure can reform in a reversible manner through dynamic bonds. Dynamic bonds are incorporated in the polymer matrix to enable self-healing function of materials and can theoretically heal unlimited times. The dynamic bonds is divided into two groups such as non-covalent bonds, which includes hydrogen bonds, π-π stacking, host-guest interactions, metal-ligand interactions, ionic interactions and van der Waals forces. The other one is dynamic covalent bonds which includes imine exchange, hindered urea bonds, boroxime bonds, disulfide bonds, Diels-Alder (DA) reaction, transesterification reaction and oxime-urethane bonds (Zhang et al., 2021).

The disulfide bonds, DA reaction, and oxime-urethane bonds are the most important dynamic covalent bonds for self-healing polyurethanes. The intrinsic