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POLYURETHANE: GREEN CHEMISTRY SYNTHESIS, APPLICATION AND BIODEGRADABILITY - A REVIEW

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ABSTRACT

Polyurethane (PU) is a type of material that links polymer diols and the isocyanate group. PUs can be functionalized to desired properties by introducing appropriate isocyanates and polyols. PUs can also be made biodegradable by incorporating plant-based polyols. The overview of isocyanates and polyols used in PUs is discussed in this paper. Typically, the synthesis of PUs is through conventional methods. However, the conventional method is both time and energy consuming hence a less time-consuming method which is known as microwave-assisted synthesis is discussed in this review. On the other hand, PUs has been used extensively in various applications such as coatings, automotive parts, biomedical field, and many more hence it will lead to pollution. Thus, the degradability of polymers is also discussed. This review provides insights into the microwave-assisted synthesis of polyurethane and various applications of PUs.

Keywords: Green chemistry, microwave-assisted synthesis, polyurethane, biodegradable polymer, polyol

INTRODUCTION

Plastics has been a part of human life since its discovery. Excessive usage of plastics has increased the pollution rate around the globe. The plastics that were used will usually end up in a landfill or sea hence it is a threat to land and aquatic lives. According to National Geographic, packaging plastics that were used once and then discarded are the main contributor to global plastic pollution [1].

However, the usage of plastics in some industries is unavoidable. The usage of polyurethane (PU) is extensive in coatings, automotive parts, biomedical parts, building and construction materials, textiles, and packaging materials. The versatility of PU has made it one of the most used polymers in the world. According to statistics, 18 million tons of PU were produced in 2016 [2]. In fact, in 2021, PU production is reported to be 57.34 billion USD [3]. Market research conducted by Grandview Research showed that the demand for PU will keep increasing until the year 2025. With the increasing demand for PU, the problem with pollution also increases.

Therefore, the idea of incorporating biodegradable materials such as polylactic acid (PLA) and vegetable oil-based polyol has sparked interest in the research and development field. Since PUs are synthesizable through a reaction between isocyanate or prepolymer and polyol, incorporating biodegradable prepolymer and polyol seems to be a great recipe to produce biodegradable PU. Polyols can be categorized into two, which are petroleum-based polyol and vegetable oil-based polyol where the latter has biodegradable properties compared to the former [4]. PLA prepolymer has been used in synthesizing PU and vegetable oil-based polyol has also been incorporated in PU synthesis. These two biodegradable materials have improved some properties of PU such as biodegradability and brittleness [5].

As the demand for PUs is increasing every year due to their various applications, a conventional method of synthesizing PU has yet to be improved. The conventional method of synthesizing PU requires a long production time relative to a microwave-assisted method. Therefore, a new method which is a microwave-assisted synthesis of PU is discussed in this review. The hypothesis is that by using microwave irradiation, less time is needed to activate the reaction energy in the synthesis of PU. If this method shows a promising future, the conventional method of synthesizing PU can be replaced with a more versatile and less time-consuming method.

SYNTHESIS OF POLYURETHANE

PU is a polymer consists of organic units, combined by carbamates (urethanes) links. PU can be produced by reacting isocyanates with polyol. Isocyanates will become a hard domain whereas polyol with diol or triol will become the soft domain in the polyurethane chain. Fig. 1 shows the chemical structure of PU.

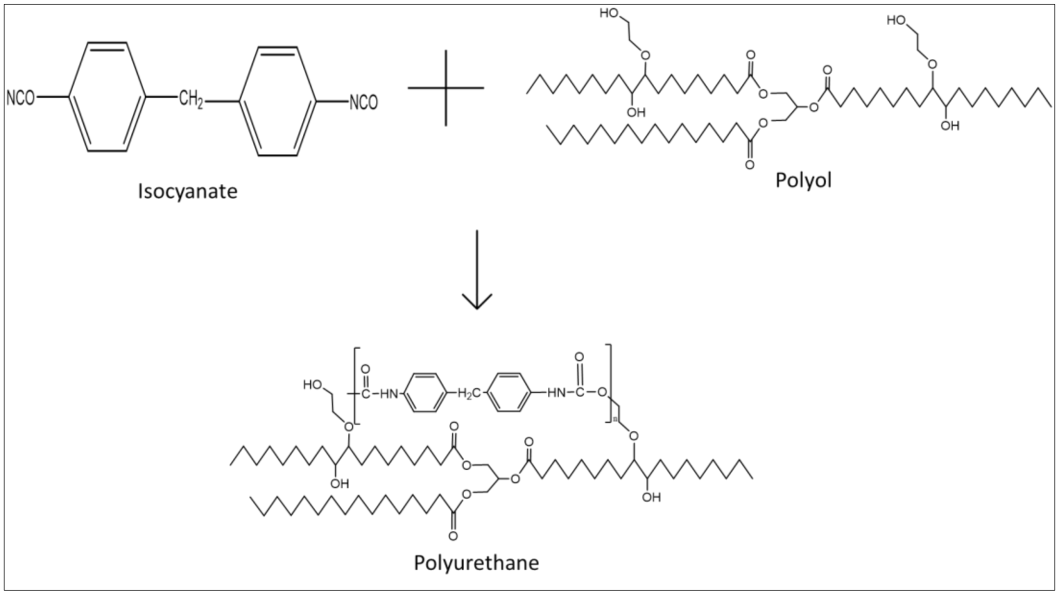


Fig. 1 Chemical structure of PU.

The polymer synthesis pathway falls into two schemes which are step-growth polymerization and chain addition polymerization. PU synthesis falls under the step-growth polymerization scheme. In step-growth polymerization scheme, it involves a stepwise build-up of monomers to dimers, tetramers, etc., until large macromolecules build-up at the end. Fig. 2 illustrates the step-growth polymerization scheme of PU. On the other hand, chain addition polymerization involves initiation, propagation, and termination steps where the large macromolecules are rapidly synthesized at the end of the termination steps [6].

$$\mathrm{R-NCO+R'-OH\rightarrow R-NH-COOR'}$$

Isocyanate – Alcohol Reaction

$$\mathrm{R-NCO+R'-NH_2\rightarrow R-NH-CO-NH-R'}$$

Isocyanate – Amine Reaction

$$\mathrm{2R-NCO+H_2O\rightarrow R-NH-CO-NH-R+CO_2}$$

Isocyanate – Water Reaction

Fig 2. PU step-growth polymerization scheme.

PU polymers are the resulting product of a step-growth polymerization reaction between isocyanates and alcohol [7]. Isocyanates can be in the form of di-isocyanates or poly-isocyanates whereas alcohol can be in the form of a diol or macro-diol. The resulting reaction between these two together with a chain extender will produce PU with a soft segment and a hard segment where polyol as the soft segment, and isocyanate and chain extender as the hard segment.

Biopolymers such as polylactic acid (PLA), cellulose, and polyhydroxy butyrate (PHB) have been used in producing polymers. PLA specifically has become the center of interest in producing PU. Lactic acid (LA) prepared into PLA diol is being used for PU synthesis. PLA can be polymerized from its monomer which is LA through polycondensation and ring-opening polymerization. PLA produced from polycondensation typically will produce low molecular weight PLA whereas PLA produced from ring-opening polymerization (ROP) will produce high molecular weight PLA [8]. ROP allows higher control of polymerization hence remains the most widely used polymerization method for the synthesis of well-defined materials [9].

To obtain PLA diol, polycondensation of LA can be done in two different ways, which are through the conventional heating method and microwave-assisted heating method. In the conventional heating method, the heating time required to achieve reaction temperature is long. As reported by Bakibaev et al. [10], through a conventional method, polycondensation requires up to 16 hours for the process to be completed at 160°C reaction temperature. In another study done by Ismail et al., [5] 6 hours of reflux time was needed to obtain PLA diol. Hence, the conventional heating method needs to be upgraded to a more sophisticated and less time-consuming method to comply with the high demand of the PU market.

Microwave-assisted Polymer Synthesis

Green chemistry is a new philosophy that is governed by the ability to minimize: (i) the use of non-renewable sources and organic solvents, (ii) generation of toxic secondary product, and (iii) the consumption of energy and gas emission [11]. Microwave-assisted synthesis (MWAS) can fulfil those criteria hence MWAS can be considered as green chemistry in polymer synthesis.

In the late 1980s, the first organic MWAS was reported [12,13]. During that time, researchers were using a conventional or domestic microwave as the reactor. However, the usage of domestic microwave made the reaction uncontrollable, and the danger of an explosion was prominent. Therefore, parallel with the advancement of technology, microwave synthesizers are now available with the custom-made option. Each research group can customize their microwave that deems suitable for their research needs.

Microwave irradiation comprises radiation with a frequency between 0.3 GHz and 300 GHz. To avoid interference with current telecommunication and radars system, most synthetic and domestic microwaves are built to operate at frequencies between 2 GHz and 8GHz, where household microwaves generally operated at 2.45 GHz frequency [14]. To fulfil the research needs, microwave instrumentation suppliers have moved towards combinatorial or high throughput medium governed by two philosophies. These two philosophies are the type of the microwave itself, known as single-mode (mono mode) and multimode microwave reactors.

In a mono mode microwave reactor, as the name suggests, only one mode is present where the electromagnetic radiation is focused directly to a reaction vessel attached at a fixed distance from the radiation source [15]. Since mono mode radiation can be accurately designed, mono mode microwave reactors are highly preferable to obtain a well-defined heating pattern for small loads [15,16]. An accurate design of radiation pattern will result in a uniform heating pattern, a criterion that is important to reach high reproducibility of a product [16].

A multimode microwave reactor is conceptually similar to a domestic microwave oven [15]. In the early stages of MWAS explorative works, most researches were done using multimode domestic microwave oven due to its affordability [17]. This type of microwave can work under constant power output and the power level is regulated by an "on-off" cycle. Other than that, microwaves that enter the cavity (rectangular metal box) undergo multiple reflections of the walls as well as a reflection by the load [15,17]. Same as mono mode microwave reactors, multimode microwave reactors can also be well-designed for larger loads. They can be equipped with power, temperature, and pressure control together with a proper venting system [16] hence making them safe and suitable for larger loads.

Numerous advantages of MWAS have made it one of the versatile synthesis methods. Problems with the conventional heating process revolved around time and energy-consuming pathways. The conventional synthesis equipment usually involves oil bath heating, sand heating, and heating mantles, where the heat produced causes the surface of the reaction vessel to be extra hot. Prolong exposure to excess heat generated would eventually lead to the decomposition of products, substrates, and reagents [16]. Conventional synthesis pathways are indeed a time and energy-consuming thus the discovery of microwave radiation ability to simplify the synthesis method is very beneficial.

Conventional heating process using an oil bath will usually result in inconsistent sample temperature. The oil bath will be heated by the heat source and heat from the oil bath will be transferred to the reaction vessel through a heat transfer method known as convection. Heat may be lost during the transfer process hence making the internal temperature inside the reaction vessels differ from the oil bath temperature. In contrast, microwave heating involves electromagnetic radiation where microwave energy is remotely introduced into a chemical reactor and passes through the reaction vessel wall, directly heating the reactants and solvents [16]. The non-contact heating mechanism will result in a higher heating rate therefore, the MWAS method can save energy yet produce higher yields in a shorter time [18].

The microwave heating mechanism is based on dielectric heating [17,18]. Dielectric heating can be defined as the ability of some polar substances (liquids and solids) to absorb and convert microwave irradiation into heat [18]. The capacity of these materials is closely associated with its dielectric properties and can be determined using loss tangent, tan δ which can be expressed in quotient $\tan \delta = \varepsilon'/\varepsilon''$. The dielectric loss denotes as ε” indicates the efficiency in which electromagnetic is converted into heat whereas dielectric constant, denote as ε’ indicates the ability of molecules to be polarized by the electric field, allowing a reasonable amount of energy to be absorbed. Therefore, to obtain high absorption efficiency for fast heating, a reaction medium with a high tan δ value is needed. However, the value of ε’ should be taken into consideration too since a high tan δ value does not necessarily mean the substances would allow reasonable energy absorption since it is depending on ε’ value.

In that sense, the solvent used for microwave synthesis can be categorized into three categories, based on their tan δ. Table 1 summarized the mentioned categories. The first category is known as high microwave absorbing where the value of tan δ is greater than 0.5. Examples of solvents under this category included ethanol, methanol, dimethyl sulfoxide, and formic acid. The second category is known as medium microwave absorbing where the value of tan δ is between 0.1 and 0.5. Acetic acid, 1,2-dichlorobenzene, dimethylformamide, and water are examples of this category. The third category is low microwave absorbing where the value of tan δ is less than 0.1, where chloroform, ethyl acetate, toluene, and hexane are examples of it. Since either substrates or some of the reagents/catalysts are likely to be polar, the overall dielectric properties of the reaction medium will in most cases permit adequate heating by microwave irradiation. However, polar additives, such as ionic liquids, can be added to otherwise low-absorbing reaction mixtures to enhance the absorbance level of the medium [18] so that the reaction can take place in optimum condition.

Table 1 Examples of solvent based on their tan δ value.

Solvent Categories	Value of tan δ	Examples of Solvent
High microwave absorbing	> 0.5	Ethanol, methanol, dimethyl sulfoxide, formic acid
Medium microwave absorbing	0.1 – 0.5	Acetic acid, 1,2-dichlorobenzene, dimethylformamide, water
Low microwave absorbing	< 0.1	Chloroform, ethyl acetate, toluene, hexane

Microwave-assisted polymerization is one of the suggested alternatives to replace the conventional heating method. Despite being newly studied, microwave-assisted polymerization shows promising results in synthesizing pre-polymer as well as the polymer itself. The microwave-assisted method can be used in preparing the pre-polymer of the desired end polymer. As an example, by using the microwave-assisted method, Bakibaev and his team managed to synthesize

PLA diol (a prepolymer) at 350W microwave power within only 10-minutes reaction time [10]. In another microwave-assisted single-step polycondensation of lactic acid, PLA diol with a weight-average molecular weight of 1800 Da was produced after being irradiated with 40W microwave power, at the reaction temperature of 200ºC and with 30 minutes of reaction time whereas tin chloride was used as the catalyst [19].

Another study on the microwave-assisted synthesis of PU had been done by Biswas and his team [20]. They successfully synthesized PU in a microwave synthesizer with the following conditions: a mixture of cyclodextrin (CD), anhydrous DMF, and toluene diisocyanate (TDI) was added together into the synthesizer vial, heated to 145ºC for 3, 6 and 10 minutes. The same mixture was also being tested with conventional heating. By using the same ratio of TDI to CD, PU was successfully synthesized using microwave synthesizer at 3-minutes reaction time with 84% yield compared to conventional heating which yielded only 74% of PU after 20-minutes reaction time [20]. In a recent study by Biswas and his team too, they were able to synthesize sucrose polyurethanes through microwave-assisted synthesis method and managed to obtain 47% yield of sucrose polyurethanes by irradiating the mixture for 6 minutes, at 145ºC reaction temperature [21]. A microwave-assisted synthesis was also being reported in synthesizing β-cyclodextrin/nitrogen-doped carbon nanotubes polyurethanes [22]. They irradiated the samples in a microwave at 700W for 10, 15, and 30 minutes. It was found that the polymerization reaction was completed in only 10 minutes of reaction time. Microwave-assisted surface functionalization between PU and poly(ethylene glycol) was also reported by You et al. [23]. Under microwave irradiation heating, they managed to achieve a 95.7% reduction of NCO surface density at only 10 minutes of reaction time with 100W microwave power compared to conventional heating, where the grafting process took 24 hours with an NCO surface reduction of 91.1% [23]. These findings proved that microwave heating able to reduce the reaction time as compared to conventional heating.

With the outstanding advantages such as non-contact heating, energy transfer instead of heat transfer, higher heating rate, rapid start-up and stopping of the heating, uniform heating with minimal thermal gradients, selective heating properties, reverse thermal effects (heating starting from the interior of the material body), energy savings and higher yields in shorter reaction time, MWAS method has become a new lifeline for polymer synthesis. The ability to rapidly produce end-product make MWAS method a new promising synthetic method in the field that requires rapid and accurate polymer synthesis, such as a biomedical field.

Isocyanates in Polyurethane Synthesis

Isocyanate is one of the main ingredients in PU synthesis. Isocyanates can be categorized into two groups based on their carbon skeleton, which are aromatic isocyanates and aliphatic isocyanates. Aromatic isocyanates are more reactive than aliphatic isocyanates [24,25]. Table 2 shows an example of isocyanates based on their respective categories.

Isocyanates in PU synthesis play an important role. Isocyanates have a functional group of (-NCO) therefore reaction between isocyanates and hydroxyl groups greatly influenced properties of PU in terms of its mechanical properties, tensile properties, and rigidity [26]. On the other hand, isocyanates in PU synthesis also responsible for chain extension and formation of urethane linkages [27]. The hard segment in PU is formed as a product of a reaction between isocyanates with a chain extender such as short-chain diols or diamines [28]. Even though another chain extender such as 1,4-butanediol being employed as a chain extender, the role of isocyanate is still significant in contributing to chain extension mechanism as well as properties of synthesized PU.

Types of isocyanates used in PU synthesis are 2,4- and 2,6-toluene diisocyanate (TDI), 4,4’-dipephenylmethane diisocyanate (MDI), and 1,6-hexamethylene diisocyanate (HDI) where TDI and MDI are the most used isocyanates because of their cost advantages and have high reactivity. Different types of isocyanates will result in different properties of PU. In producing semi-rigid and rigid PU plastic for construction and insulation purposes, MDI is commonly used. MDI also has relatively low human toxicity and the least hazardous isocyanates however they are malignant. On the other hand, TDI is used to manufacture flexible foams for furniture and automotive parts. When using isocyanates, the properties of PU can be enhanced by reducing the volatility and toxicity of isocyanates. Isocyanate volatility and toxicity can be reduced by partially reacting with polyols or by adding other materials. Hence, with reduced volatility and toxicity, isocyanates can be said safe to use by humans [8].

As mentioned, HDI, MDI, and TDI are widely used. As mentioned earlier, different types of isocyanates will result in different properties of PU. In a study of PU synthesis where both HDI and TDI were being used, PU with TDI as its source of isocyanate shows glassy and brittle behaviour whereas PU with HDI as its source of isocyanate shows flexible and rubbery behaviour [5]. In another study done by Zhang and his colleagues [29], by coupling HDI with polycaprolactone (PCL) and using acetyl tributyl acetate as plasticizers showed that the flexibility of PU thin film can be improved. These studies show that isocyanates used in synthesizing PU are dependent on the application of the said PU therefore it is crucial to test which isocyanates will give the best-desired properties to PU.

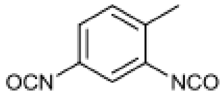
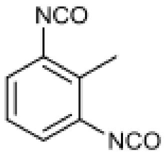
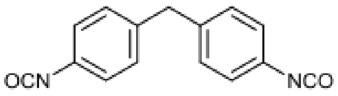
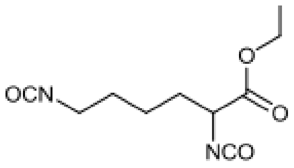
Polyols in Polyurethane Synthesis

Polyols contribute to the soft segment of PU. The reaction of polyols and isocyanates produced a PU matrix. Over the past decade, PU was made through the usage of petroleum-based polyols. However, concerns arise when petroleum sources are definite and will cease into extinction in the future. Another bigger concern of using petroleum-based polyols is the polymer produced has low biodegradability. Most of the plastic wastes will end up in landfills and the ocean thus these non-biodegradable polymers are a major threat to the earth's ecosystem. Therefore, these petroleum-based polyols are slowly being substituted with vegetable oil-based polyols which have biodegradable properties. Since vegetable oil-based polyols are biodegradable, the soft segment of polyols in the PU matrix can be adjusted to be more biodegradable thus producing biodegradable polymers.

In the current research trend, rapeseed oil, sunflower oil, soybean oil, canola oil, and castor oil have been successfully derived and applied in the synthesis of flexible PU [30–33]. The properties of PU made from the mentioned vegetable oil-based polyols are also being studied. On the other hand, in the Malaysia research scenario, Malaysian Palm Oil Board (MPOB) has started using palm oil-based polyols in their production of PU [34]. Many PU products have been developed from rigid and flexible PU foams [35]. Palm oil-based polyols were also found to be suitable for the production of coatings, adhesives, and elastomers [36,37]. Since palm oil can be easily obtained in Malaysia and available in abundance, this renewable feedstock should be fully utilized thus making Malaysia the main producer of biodegradable PU in the future.

As previously mentioned, PUs can be categorized into two major groups which are flexible PU and rigid PU. The amount of soft segment from polyols in PU synthesis contributes to PU formation. In a study done by Dworakowska and team [30], rapeseed oil-based polyol was synthesized in two methods which are epoxidation and microwave-assisted ring-opening polymerization. It is worth mentioning that applying microwave irradiation allowed the reaction time to be shortened. Rapeseed oil polyols were mixed in a well-established formulation for PU foam synthesis. The elongation at break and tensile properties of rapeseed oil-based PU were lower thus make the PU flexible [30].

Table 2 Examples of isocyanates used in PU synthesis.

Group of Isocyanates	Name of Isocyanates	Chemical Structure
Aromatic	2,4-Toluene diisocyanate (TDI)	
	2,6-Toluene diisocyanate (TDI)	
	4,4'-Diphenylmethane diisocyanate (MDI)	
Aliphatic	1,6-Hexamethylene diisocyanate (HDI)	
	L-Lysine ethyl ester diisocyanate (LDI)	

In another study conducted by Acik and team [38], epoxidized soybean oil (ESBO) was used to produce PU. ESBO was further treated in the hydroxylation process with resulting ESBO with a hydroxyl number of 300 mg KOH/g. Treated ESBO was then included in the formulation of PU films. The authors reported that tensile strength, elongation at break, and Young's modulus of PU films increased as the ratio of isocyanate content to ESBO increased. Therefore, the authors concluded that the mechanical properties of soybean oil-based PU films were enhanced with the increase of isocyanate content [38].

Meanwhile, Macalino and team [39] used castor oil to synthesize PU film. The reaction of castor oil and 1,6-hexamethylene diisocyanate (HDI) resulted in PU film formation. PU films were synthesized with different ratios of castor oil to isocyanate. Tensile properties of castor oil-based PU were characterized and the findings showed that all PU films were flexible and the flexibility increased as the castor oil content increased. The author stated that since castor oil contributes to the soft segment of PU, high castor oil contents resulted in flexible PU. On the other hand, the tensile strength of PU films was directly proportional to HDI. Since HDI contributes to the hard segment of PU films thus HDI was responsible for PU hardness. The researchers concluded that PU with more HDI contents was stiff and inelastic whereas PU with less HDI contents was soft and flexible [39].

Palm oil-based polyol had been used to synthesize PU [40]. Their team successfully synthesized palm oil-based polyol using two steps which are epoxidation and oxirane ring-opening. The resulting palm oil-based polyol was included in PUs foams formulation. Palm oil-based polyols were mixed with petrochemical polyols thus PUs foam produced contain both petrochemical polyols and bio-based polyols. Mechanical properties which are tensile strength and elongation at break were studied. Pawlik and team [40] reported that PUs foam modified with polyols have high tensile strength compared to PUs foam with petrochemical polyol. They also reported that elongation at break for PUs foam modified with palm oil-based polyols was increased. They claimed that substituting petrochemical polyols with palm oil-based polyols allowed improvement of selected properties for PUs [40].

Replacing polyether polyols with natural palm olein polyol showed a promising result in viscoelastic (memory) PU foams, according to Nurul ‘Ain et al., [41]. Incorporating palm oil polyol in the formation of viscoelastic foam increased foaming rate, increased PU foam cells, and load bearing of the PU foam as well as increased tear strength. All these characteristics are important when producing viscoelastic PU foams for bedding application. In a different study done by Adnan and the team, they were able to produce PU foams with high energy absorption when using palm olein polyol in their formulation [42]. High energy absorption is one of the important factors in automotive seat cushions. Another important property in automotive seating application is hysteresis. Lower hysteresis indicates high durability of high resilience PU foams [43], and Adnan et al., has proven that by incorporating palm oil polyol managed to do so [42].

From the above examples, it can be said that bio-based polyols can increase and improve the properties of PUs. Other than being biodegradable, bio-based polyols are from renewable feedstock thus they are always available when needed. Malaysia is the second-largest palm oil producer in the world therefore by utilizing palm oil resources in PUs synthesis would give rise to national economic value and eventually will make Malaysia one of the manufacturers of biodegradable PUs in the world.

DEGRADABILITY OF POLYMER

Degradation of polymers can be categorized into thermal degradation, chemical degradation, mechanical degradation, photodegradation, and biodegradation. Thermal degradation occurs when heat or elevation of temperature on a polymer causes loss of polymer properties (such as electrical, physical, and mechanical properties). Thermal degradation can also be defined as molecular deterioration due to overheating [44]. In general, the conventional thermal degradation model is based on an autoxidation process. In the autoxidation process, initiation, propagation, and termination are the major steps involved.

However, it is worth mentioning that degradation steps are not the reversal of polymerization steps even though degradation reaction steps are the same as polymerization reaction steps [45]. A degradation study on polymer behavior (polyethylene, polypropylene, and polystyrene) conducted by Murata et al. indicated that two reactions have simultaneously occurred during the degradation process. Those reactions are random scission of chain links which caused molecular weight reduction of the raw polymer and, chain-end scission of C-C bonds which generate volatile product [46]. In the thermal degradation process, the energy required for the reaction to take place depends on the branching of the polymers. Polymers with extensive branches require less activation energy compared to polymers with little branches [47]. Therefore, polymers that have extensive branches such as low-density polyethylene will thermally degrade quickly compared to high-density polyethylene.

Chemical degradation of polymers includes hydrolysis, alcoholysis, acidolysis, glycolysis, and aminolysis. Chemical degradation can be defined as full depolymerization of polymer to the monomers, or partial depolymerization to oligomers and other chemical substances. Since polymers are made of many organics and inorganics constituents, they can be cleaved by using reagents such as water, alcohol, acids, glycol, and amines. Hydrolysis uses water as the reagent in the process, whereby the polymers are depolymerized either in the alkaline, acidic, or neutral condition in the presence of water. However, hydrolysis is a slow process and requires high pressure and temperature. Despite being slow in the process, hydrolysis is capable of producing virgin monomers and some other chemicals [48]. Alcoholysis is a degradation of the polymer in the presence of a catalyst and low molecular weight alcohol. Alcoholysis is very efficient when reaction temperature and reaction time are low. PU foams when undergone alcoholysis will produce polyol and amine compounds. These two compounds can be used again as a raw material for PU product preparation [49].

Acidolysis is another process for PU degradation. As the process name suggests, acidolysis uses organic and inorganic acid for PU degradation. Inorganic acids can decompose urethane links in PU into amine salts and polyol. On the other hand, the usage of unsaturated aliphatic acids such as maleic acid and fumaric acid can transform the urethane groups into amides. Dicarboxylic acid such as adipic acid can be used as a cleavage reagent where the products of this reaction are amine salts, amides, oligoureas, amine salts, and polyols. These products can be used again in PU preparation after neutralization treatment [45]. Glycolysis involves transesterification of carbamate group in PU with glycol solvents. It can be done with or without catalyst and it is a single-step reaction. The by-products obtained are aromatic amines and long-chain polyols. In a study conducted by Sendijarevic, a mixture of TDI and polymeric methylene diphenyl diisocyanate-based foams were able being synthesized by using recycled polyols [50]. Meanwhile, in the aminolysis process, pure polyols components can be recovered by reacting PU with either aliphatic monoamine or polyamines [51].

In polymer biodegradation, polymeric materials are broken down into smaller compounds by naturally occurring microorganisms such as algae, bacteria, and fungi [52]. The biodegradation process also depends on environmental factors such as temperature, humidity, and pH [53]. Polymer biodegradation can be explained in two steps. The first step in polymer biodegradation is known as defragmentation where heat, moisture, and microbial enzymes initiated the process. The second step is where longer molecular compounds are changed into smaller compounds. Naturally occurring acids and enzymes are responsible for second step initiation. Therefore, it is important to study the biodegradation of polymers in the sense that the polymer produced will either last long or degrade quickly, depending on polymer application.

As mentioned in the previous paragraph, the biodegradability of polymer does not only depend on the environmental factors but also depends on polymer chemical structures and the origin of the polymer [45]. Thus, polymer biodegradation can be categorized into three groups. The first group is a mixture of synthetic polymer and substances that can be easily digested by the microorganism. Examples of polymers are modified natural polymer and a natural polymer such as starch and cellulose. The second group is a synthetic polymer such as PCL that has a functional group susceptible to hydrolytic attack and the third group is a biopolymer made of bacterial sources. These three groups of polymers would have a high capability for degradation [54].

In packaging material and biomedical applications, the polymer should be degraded fast enough to lessen the pollution and to reduce foreign body reactions in the case of biomedical implants [55]. On the other hand, in the applications of sealants, adhesives, and coatings, the polymer should not be affected much by ultraviolet (UV) degradation and weathering. Different polymer application requires a vast understanding of polymer degradation thus degradation study serves as a platform to narrow the knowledge gap. Since there are few ways for polymer degradation, identifying which preferable degradation pathway will help in designing polymers with desirable degradation properties.

POLYURETHANE AND ITS APPLICATION

Due to its versatility, PU has been used in various applications including coatings, automotive parts, biomedical parts, building and construction materials, textiles, and packaging materials. PUs can be classified into few categories such as PU foams, elastomers, and thermoplastic PU (TPU). PU coatings are outstanding due to their ability to well-adhered to a wide variety of base materials. With properties such as water resistance, abrasion resistance, and weather resistance, PU coatings are widely used. PU coatings can also be used in the marine coating due to their high abrasion resistance and waterproofness [56]. However, care must be taken since prolonging the exposure of PU coatings to ultraviolet (UV) light might degrade the coatings themselves. Despite being prone to UV degradation, additives such as UV absorbers can be added to PU coating to make PU coating more resistant to UV, thus can be used to coat surfaces that may require light stability.

PU foams can be either low-density flexible foams or low-density rigid foams [57]. Furniture, automotive seating, cushions, and bedding are mostly from low-density flexible PU foams. Flexible PU foams have high mechanical strength, resilience, and durability. On the other hand, rigid foams PU are used as a core material in building insulator panels and manufacturing refrigerators. Rigid PU foams govern the properties of high mechanical strength, low density, low heat conduction, and low moisture absorption. As PU foams are capable as an insulator, collaboration research between MPOB, InterMed Sdn. Bhd. and Lafarge Group succeeded to produce palm oil-based PU foams for ceiling panels, Monier CoolBoard [58]. The product was a part of the Monier CoolRoof system, was tested for its ability to reduce heat transmission from the roof to the room. As predicted, Monier CoolBoard was able to reduce daily heat transmission up to 87% and the additional cost for incorporating the CoolRoof concept was estimated to be 0.5% up to 2% of the total building cost [58]. For a tropical country like Malaysia, this type of cooling system is very ideal to be implemented since it will cut the cost of using air-conditioning as well as able to reduce pollution caused by the usage of excessive air-conditioning.

One of thermoplastic polyurethane (TPU) properties is high abrasion resistance. This property makes TPU preferable to be used in the production of automotive parts such as gear knobs, instrument panels, console parts whereas high resilience flexible PU foams are used in a car seat. These automotive parts are produced with PU by using reaction-injection moulding (RIM). Surface quality, aging, abrasion, and scratch resistance are highly needed in automotive parts production. TPUs could fulfil those stringent requirements while being economical. Since TPU is a PU with alternating hard segment and soft segment, properties of TPU can be designed according to desired properties where the alternating hard and soft segment can be controlled during the synthesis process. Therefore, the usage of TPU with desirable properties in the automotive industry is in high demand [59].

PU elastomer is the other classification of PU and is considered as a substitute for plastic and rubber. They possess properties of high compression strength, resistance to high loads, and have a low cost. PU elastomers also can be easily formulated and coloured, hence they are preferable in the manufacturing of packaging materials, health products, and the printing industry. In the footwear industry, low-density elastomers are used to manufacture shoe soles [60].

On the other hand, PUs also has become an interest in the biomedical field. For PUs to be used in the biomedical field, PUs must possess both biocompatibility and biostability. In *in vivo* study done by Lehle et al., they cultivated human saphenous vein endothelial cells (HSVEC) and a mouse fibroblast cell line (L-929) with various commercially available PU. The results of their study concluded that commercially available PU was not favourable for colonization of patient-derived HSVEC, where PU surface modification is needed to favour such colonization [61]. Generally, PUs are made up of alternating soft segments and hard segments of isocyanate and polyol. Takahara et al. reported that the hard segments of PUs were highly thrombogenic in platelet retention experiments [62], making any PU without modification is prone to cause blood clotting if being used *in vivo*.

To overcome these problems, a lot of modification studies have been done to improve the biocompatibility of PUs. Han et al. had use L-lysine diisocyanate-based PU and L-lysine as the chain extender of the PU. The PU scaffolds were prepared through electrospinning. The results of the studies showed that HSVECs and L-929 cells were well attached and visible on PUs scaffolds [63]. Pereira and the team succeeded in synthesizing a photo-polymerizable and injectable PU for biomedical application. *In vitro* results of the test showed that the synthesized PUs were cytocompatible, meanwhile *in vivo* results of the test showcased good biocompatibility during 4 weeks [64]. From the mentioned studies, even though PUs are not readily biocompatible however, a lot of improvement can be made to make PUs biocompatible hence allowing them to be used in the biomedical field.

In the case of biostability, this issue has always been a concern for PUs, therefore most of the PU-based medical devices are used only for the short term. It is well-known that polyester-based PUs are not stable in water and oxygen, therefore, most of the medical-grade PUs in the market are either polyether-based or polycarbonate-based [65]. However, experiments using polyether-based or polycarbonate-based PUs show that these types of PUs are not stable i*n vivo* and as a result, pacemakers made of these PUs were withdrawn from the market [66]. The biostability of PUs is very important for long-term usage of PUs. Hence, many modifications were attempted to enhance PUs biostability accordingly. In their study, Wiggins et al. had found that the soft segment of PUs played an important role in PUs biostability [67], therefore a lot of PUs modifications were made based on this important finding. These modifications included replacing a soft segment of PUs with more stable materials such as polyolefins and polysiloxane [68,69], by doing surface modification of PUs [70], by incorporating nanoparticles [71,72] and by incorporating antioxidants [73].

Biocompatibility and biostability are indeed among important criteria for PUs to be used in biomedical applications, but biodegradable PUs with controlled degradation rates [74] are also desirable in drug delivery, short-term implants, and scaffolds application. PU scaffold itself is the ideal drug carrier for a local controlled drug delivery system. Moon and his team had conducted a study where heparin-deoxycholic acid (DOCA) conjugate was loaded into a PU film by solvent casting. At the end of the experiments, it was discovered that when heparin-DOCA was loaded above 7.5% into PU film, the release of heparin-DOCA was able to prevent the formation of a fibrin clot and platelet adhesion on the film surface [75]. As heparin is known as an injectable anticoagulant reagent in medical practice, Chen et al. have conducted a study on heparin-mimetic PU hydrogel. The heparin-mimetic hydrogel was synthesized by introducing sulphated konjac glucomannan (SKGM) into the recipe. The mimetic hydrogel showed prolong activated partial thromboplastin time and thromboplastin time, therefore strengthen the ability of PU hydrogel in preventing blood clot formation [76]. In another study done by Hafeman and team, they succeeded in designing injectable PU scaffolds incorporated with tobramycin by reactive liquid moulding where the released tobramycin remained biologically active against *Staphylococcus aureus* [77]. Isocyanates have wide reactivity thus many drugs can be chemically bonded into the main chain of PUs instead of physically blended. The release of the drugs could be achieved by the degradation of PUs. Kenawy et al. managed to design PUs containing azo-linked polymeric prodrugs of 5-aminosalicylic acid (5-ASA) in the main chain of PUs, where the hydrolysis of the urethane bond in the main chain triggered the release of the drugs [78]. From mentioned proofs, it shows that PU is suited to be one of the biomaterials used in daily life.

CONCLUSION

The synthesis method of PUs is moving towards a greener method, which is microwave-assisted synthesis. Microwave-assisted synthesis of PUs provides numerous advantages compared to the conventional method. With a less time-consuming method, more PUs can be produced in a shorter period. This will increase the production of PUs. In 2019, the International Union of Pure and Applied Chemistry (IUPAC) has published a list of ten emerging technologies in Chemistry with the potential to make our planet more sustainable. The technologies that enable the transformation of plastic into monomer have become the topic of interest. The technologies eventually will allow the reduction of plastic waste and reducing the usage of fossil fuels. Microwave-assisted synthesis can be considered as one of the said emerging technologies. A lot more to be discovered in microwave-assisted synthesis especially in PU synthesis thus a continuous study should be done to fully exploit the advantages of using the green synthesis method.

The biodegradability of PUs can be enhanced by introducing natural-based polyols such as palm oil polyol, castor oil polyol, and epoxidized soybean oil. By incorporating these types of polyols is proven to enhance the biodegradability of PUs. Therefore, producing biodegradable PU has always become the main interest of polymer researchers worldwide. Other than that, PUs can be designed to fulfil the criteria for each application. For example, surface modification of PUs can be made to make them more biocompatible for biomedical use. The hydrolysis of the PUs in the main branch can be exploited in designing a controlled release of drugs in the drug delivery system.

Incorporating biodegradable materials coupled with a microwave-assisted method in polymer synthesis is expected to be one of the powerful tools in the polymer field. Along with technological advancement, it is expected that soon, rapid polymer synthesis will be a common sight and human beings can use plastic without having to think of pollution since most of the plastics are already biodegradable.

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REFERENCES

[1] Parker L. Facts About Plastic Pollution. *Natl Geogr Mag* 2018.
[2] Furtwengler P, Boumbimba RM, Avérous L. Elaboration and Characterization of Advanced Biobased Polyurethane Foams Presenting Anisotropic Behavior. *Macromol Mater Eng* 2018;303:1–11.
[3] Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR. Polyurethane types, synthesis and applications-a review. *RSC Adv* 2016;6:114453–82.
[4] Haryono A, Triwulandari E, Sondari D, Randy A, Ridwanuloh AM. Control of Biodegradability of Polyurethane Foam Based on Palm Oil by Ratio of Soft Segment on the Polymer Backbone. *J Biotek* 2005:11–7.
[5] Ismail MN, Rafidi N, Awale RJ, Ali F. Preparation and characterization of polylactic acid based polyurethane for environmental friendly packaging materials. *J Adv Res Fluid Mech Therm Sci* 2017;38:16–21.
[6] Obi BE. Polymer Chemistry and Synthesis. *Polym Foam Struct* 2018:17–40.
[7] Sonnenschein MF. Polyurethanes: Science, Technology, Markets, and Trends. *Polyurethanes Sci Technol Mark Trends* 2014;9781118737:1–417.
[8] Ali FB, Ismail N. Polymerization Methods and Characterizations for Poly(Lactic Acid) (PLA) Based Polymers. *Multifaceted Protoc Biotechnol* 2018:139–50.
[9] Dechy-Cabaret O, Martin-Vaca B, Bourissou D. Controlled ring-opening polymerization of lactide and glycolide. *Chem Rev* 2004;104:6147–76.
[10] Bakibaev AA, Gazaliev AM, Kabieva SK, Fedorchenko VI, Guba GY, Smetanina EI, et al. Polymerization of Lactic Acid Using Microwave and Conventional Heating. *Procedia Chem* 2015;15:97–102.
[11] Tucker JL. Green chemistry: Cresting a summit toward sustainability. *Org Process Res Dev* 2010.
[12] Gedye R, Smith F, Westaway K, Ali H, Baldisera L, Laberge L, et al. The use of microwave ovens for rapid organic synthesis. *Tetrahedron Lett* 1986;27:279–82.
[13] Giguere RJ, Bray TL, Duncan SM, Majetich G. Application of commercial microwave ovens to organic synthesis. *Tetrahedron Lett* 1986;27:4945–8.
[14] Kappe CO. Controlled microwave heating in modern organic synthesis. *Angew Chemie -*

Int Ed 2004;43:6250–84.

[15] Kappe CO. High-speed combinatorial synthesis utilizing microwave irradiation. *Curr Opin Chem Biol* 2002;6:314–20.

[16] Mavandadi F, Pilotti Å. The impact of microwave-assisted organic synthesis in drug discovery. *Drug Discov Today* 2006;11:165–74.

[17] Sosnik A, Gotelli G, Abraham GA. Microwave-assisted polymer synthesis (MAPS) as a tool in biomaterials science: How new and how powerful. *Prog Polym Sci* 2011;36:1050–78.

[18] Mallakpour S, Rafiee Z. New developments in polymer science and technology using combination of ionic liquids and microwave irradiation. *Prog Polym Sci* 2011;36:1754–65.

[19] Nagahata R, Sano D, Suzuki H, Takeuchi K. Microwave-assisted single-step synthesis of poly(lactic acid) by direct polycondensation of lactic acid. *Macromol Rapid Commun* 2007;28:437–42.

[20] Biswas A, Appell M, Liu Z, Cheng HN. Microwave-assisted synthesis of cyclodextrin polyurethanes. *Carbohydr Polym* 2015;133:74–9.

[21] Biswas A, Kim S, Gómez A, Buttrum M, Boddu V, Cheng HN. Microwave-Assisted Synthesis of Sucrose Polyurethanes and Their Semi-interpenetrating Polymer Networks with Polycaprolactone and Soybean Oil. *Ind Eng Chem Res* 2018;57:3227–34.

[22] Masinga SP, Nxumalo EN, Mamba BB, Mhlanga SD. Microwave-induced synthesis of β-cyclodextrin/N-doped carbon nanotube polyurethane nanocomposites for water purification. *Phys Chem Earth* 2014;67–69:105–10.

[23] You D, Liang H, Mai W, Zeng R, Tu M, Zhao J, et al. Microwave-assisted functionalization of polyurethane surface for improving blood compatibility. *J Ind Eng Chem* 2013;19:1587–92.

[24] Iqbal N, Tripathi M, Parthasarathy S, Kumar D, Roy PK. Aromatic versus Aliphatic: Hydrogen Bonding Pattern in Chain-Extended High-Performance Polyurea. *ChemistrySelect* 2018;3:1976–82.

[25] Prisacariu C. Polyurethane Elastomers : From Morphology to Mechanical Aspects. Polyurethane Elastomers *From Morphol to Mech Asp* 2011.

[26] Petrović ZS, Zhang W, Zlatanić A, Lava CC, Ilavský M. Effect of OH/NCO molar ratio on properties of soy-based polyurethane networks. *J Polym Environ* 2002;10:5–12.

[27] Petrović ZS, Ferguson J. Polyurethane elastomers. *Prog Polym Sci* 1991;16:695–836.

[28] Hepburn C. Property-Structure Relationships in Polyurethanes 1992:51–106.

[29] Zhang Y, Wang J, Fang X, Liao J, Zhou X, Zhou S, et al. High solid content production of environmentally benign ultra-thin lignin-based polyurethane films: Plasticization and degradation. *Polymer (Guildf)* 2019.

[30] Dworakowska S, Bogdal D, Prociak A. Microwave-assisted synthesis of polyols from rapeseed oil and properties of flexible polyurethane foams. *Polymers (Basel)* 2012;4:1462–77.

[31] Ghasemlou M, Daver F, Ivanova EP, Adhikari B. Polyurethanes from seed oil-based polyols: A review of synthesis, mechanical and thermal properties. *Ind Crops Prod* 2019;142:111841.

[32] Tan ACW, Polo-Cambronell BJ, Provaggi E, Ardila-Suárez C, Ramirez-Caballero GE, Baldovino-Medrano VG, et al. Design and development of low cost polyurethane biopolymer based on castor oil and glycerol for biomedical applications. *Biopolymers*

2018;109:1–10.

[33] Zhang C, Kessler MR. Bio-based polyurethane foam made from compatible blends of vegetable-oil-based polyol and petroleum-based polyol. *ACS Sustain Chem Eng* 2015;3:743–9.

[34] Ooi T, Salmiah a, Hazimah A, Chong Y. An overview of R&D in palm oil-based polyols and polyurethanes in MPOB. *Palm Oil Dev* 2006;44:1–7.

[35] Hanzah NA, Noor T, Tuan M, Adnan S, Noor NM, Polyols PO. Development of Palm Oil-based Polyols and Polyurethane Products in MPOB 2019;71:13–7.

[36] Hazimah AH, Hoong SS, Mohd Norhisham S, Tuan Noor Maznee TI, Friebel S, Philipp C, et al. Palm-Based Polyol for Adhesive. *MPOB Inf Ser* 2005:MPOB TT No. 277.

[37] Mohd Norhisham S, Tuan Noor Maznee TI, Nurul Ain H, Kosheela Devi PP, Srihanum A, Norhayati MN, et al. Soft polyurethane elastomers with adhesion properties based on palm olein and palm oil fatty acid methyl ester polyols. *Int J Adhes Adhes* 2017;73:38–44.

[38] Acik G, Karabulut HRF, Altinkok C, Karatavuk AO. Synthesis and characterization of biodegradable polyurethanes made from cholic acid and L-lysine diisocyanate ethyl ester. *Polym Degrad Stab* 2019;165:43–8.

[39] Macalino AD, Salen VA, Reyes LQ. Castor Oil Based Polyurethanes: Synthesis and Characterization. *IOP Conf Ser Mater Sci Eng* 2017;229.

[40] Pawlik H, Prociak A. Influence of Palm Oil-Based Polyol on the Properties of Flexible Polyurethane Foams. *J Polym Environ* 2012;20:438–45.

[41] Nurul ‘Ain H, Maznee TITN, Norhayati MN, Noor MAM, Adnan S, Devi PPK, et al. Natural Palm Olein Polyol as a Replacement for Polyether Polyols in Viscoelastic Polyurethane Foam. *JAOCS, J Am Oil Chem Soc* 2016;93:983–93.

[42] Adnan S, Tuan Noor MTI, Ain NH, Devi KPP, Mohd NS, Shoot Kian Y, et al. Impact of the hard-segment concentration on highly resilient polyurethane foams based on palm olein polyol. *J Appl Polym Sci* 2017;134:1–10.

[43] McEvoy JT. Advances in polyurethane foam property control. *SAE Tech Pap* 2001.

[44] Beyler CL, Hirschler MM. Thermal Decomposition of Polymers. *Chem Mater* 2011;23:3495–508.

[45] Bhuvaneswari. G H. Degradability of Polymers. *Elsevier Inc.*; 2018.

[46] Murata K, Hirano Y, Sakata Y, Uddin MA. Basic study on a continuous flow reactor for thermal degradation of polymers. *J Anal Appl Pyrolysis* 2002;65:71–90.

[47] Park JW, Oh SC, Lee HP, Kim HT, Yoo KO. A kinetic analysis of thermal degradation of polymers using a dynamic method. *Polym Degrad Stab* 2000;67:535–40.

[48] Bartolome L, Imran M, Gyoo B, A. W, Hyun D. Recent Developments in the Chemical Recycling of PET. *Mater Recycl - Trends Perspect* 2012.

[49] Yang W, Dong Q, Liu S, Xie H, Liu L, Li J. Recycling and Disposal Methods for Polyurethane Foam Wastes. *Procedia Environ Sci* 2012;16:167–75.

[50] Sendijarevicy V. Chemical recycling of mixed polyurethane foam stream recovered from shredder residue into polyurethane polyols. *J Cell Plast* 2007;43:31–46.

[51] Zia KM, Bhatti HN, Ahmad Bhatti I. Methods for polyurethane and polyurethane composites, recycling and recovery: A review. *React Funct Polym* 2007;67:675–92.

[52] Pandey JK, Takagi H, Nakagaito AN, Saini DR, Ahn SH. An overview on the cellulose based conducting composites. *Compos Part B Eng* 2012;43:2822–6.

[53] Doğan Atik I, Özen B, TIhmInlIoğlu F. Water vapour barrier performance of corn-zein

coated polypropylene (PP) packaging films. *J Therm Anal Calorim* 2008;94:687–93.
[54] Leja K, Lewandowicz G. Polymer biodegradation and biodegradable polymers - A review. *Polish J Environ Stud* 2010;19:255–66.
[55] Anderson JM, Rodriguez A, Chang DT. Foreign body reaction to biomaterials. *Semin Immunol* 2008;20:86–100.
[56] Bleile H, Rodgers SD. Marine Coatings. Encycl. *Mater. Sci. Technol.*, 2001, p. 5174–85.
[57] Szycher M. *Szycher's handbook of polyurethanes: Second edition*. 2012.
[58] Hazimah AH, Kosheela Devi PP, Tuan Noor Maznee TI, Mohd Norhisham S, Hoong SS, Yeong SK, et al. Palm-based Polyols and Polyurethanes : Two Decades of Experience. *Oil Palm Bull* 2011;63:33–42.
[59] Miller LJ, Sawyer-Beaulieu S, Tam E. Impacts of Non-Traditional Uses of Polyurethane Foam in Automotive Applications at End of Life. *SAE Int J Mater Manuf* 2014;7:711–8.
[60] Peng P, Ding S, Wang Z, Zhang Y, Pan J. Acute effect of engineered thermoplastic polyurethane elastomer knockoff running footwear on foot loading and comfort during heel-to-toe running. *Gait Posture* 2020;79:111–6.
[61] Lehle K, Stock M, Schmid T, Schopka S, Straub RH, Schmid C. Cell-type specific evaluation of biocompatibility of commercially available polyurethanes. *J Biomed Mater Res - Part B Appl Biomater* 2009;90 B:312–8.
[62] Takahara A, Tashita J ichi, Kajiyama T, Takayanagi M, MacKnight WJ. Microphase separated structure, surface composition and blood compatibility of segmented poly(urethaneureas) with various soft segment components. *Polymer (Guildf)* 1985;26:987–96.
[63] Han J, Cao RW, Chen B, Ye L, Zhang AY, Zhang J, et al. Electrospinning and biocompatibility evaluation of biodegradable polyurethanes based on L -lysine diisocyanate and L -lysine chain extender. *J Biomed Mater Res - Part A* 2011;96 A:705–14.
[64] Pereira IHL, Ayres E, Patrício PS, Góes AM, Gomide VS, Junior EP, et al. Photopolymerizable and injectable polyurethanes for biomedical applications: Synthesis and biocompatibility. *Acta Biomater* 2010;6:3056–66.
[65] Wang W, Wang C. Polyurethane for biomedical applications: A review of recent developments. *Elsevier Masson SAS.*; 2012.
[66] Vermette P, Griesser HJ, Laroche G, Guidoin R. I NTELLIGENCE U NIT 6 *Biomedical Applications of Polyurethanes.* 2001.
[67] Wiggins MJ, MacEwan M, Anderson JM, Hiltner A. Effect of soft-segment chemistry on polyurethane biostability during in vitro fatigue loading. *J Biomed Mater Res - Part A* 2004;68:668–83.
[68] Cozzens D, Ojha U, Kulkarni P, Faust R, Desai S. Long term in vitro biostability of segmented polyisobutylene-based thermoplastic polyurethanes. *J Biomed Mater Res - Part A* 2010;95:774–82.
[69] Kang J, Erdodi G, Brendel CM, Ely D, Kennedy JP. Polyisobutylene-based polyurethanes. V. oxidative-hydrolytic stability and biocompatibility. *J Polym Sci Part A Polym Chem* 2010;48:2194–203.
[70] Ward R, Anderson J, McVenes R, Stokes K. In vivo biostability of polyether polyurethanes with fluoropolymer and polyethylene oxide surface modifying endgroups; resistance to metal ion oxidation. *J Biomed Mater Res - Part A* 2007.
[71] Chou CW, Hsu SH, Chang H, Tseng SM, Lin HR. Enhanced thermal and mechanical

properties and biostability of polyurethane containing silver nanoparticles. P*olym Degrad Stab* 2006;91:1017–24.

[72] Hsu SH, Chou CW. Enhanced biostability of polyurethane containing gold nanoparticles. *Polym Degrad Stab* 2004;85:675–80.

[73] Stachelek SJ, Alferiev I, Ueda M, Eckels EC, Gleason KT, Levy RJ. Prevention of polyurethane oxidative degradation with phenolic antioxidants covalently attached to the hard segments: Structure-function relationships. *J Biomed Mater Res - Part A* 2010;94:751–9.

[74] Guelcher SA. Biodegradable polyurethanes: Synthesis and applications in regenerative medicine. *Tissue Eng - Part B Rev* 2008;14:3–17.

[75] Tae Moon H, Lee YK, Koo Han J, Byun Y. A novel formulation for controlled release of heparin-DOCA conjugate dispersed as nanoparticles in polyurethane film. *Biomaterials* 2001;22:281–9.

[76] Chen Y, Wang R, Wang Y, Zhao W, Sun S, Zhao C. Heparin-mimetic polyurethane hydrogels with anticoagulant, tunable mechanical property and controllable drug releasing behavior. *Int J Biol Macromol* 2017;98:1–11.

[77] Hafeman AE, Zienkiewicz KJ, Carney E, Litzner B, Stratton C, Wenke JC, et al. Local delivery of tobramycin from injectable biodegradable polyurethane scaffolds. *J Biomater Sci Polym Ed* 2010;21:95–112.

[78] Kenawy ER, Al-Deyab S, El-Newehy MH. Controlled release of 5-Aminosalicylic acid (5-asa) from new biodegradable polyurethanes. *Molecules* 2010;15:2257–68.