PREPARATION AND CHARACTERIZATION OF HYDROPHOBIC POLYURETHANE COATING FOR STEEL SURFACES

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PREPARATION AND CHARACTERIZATION OF HYDROPHOBIC POLYURETHANE COATING FOR STEEL SURFACE

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DECLARACTION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “**Preparation and characterization of hydrophobic polyurethane coating for steel surfaces**”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF SYMBOLS

%	Percentage
wt.%	Weight Percentage
°	Degree
°C	Degree Celsius
mm	Millimetre
nm	Nanometre

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
Al	Aluminium
Al_2O_3	Aluminium Oxide
FTIR	Fourier Transform Infrared Spectroscopy
GNP	Graphene nanoplatelets
HCl	Hydrochloric acid
HNO3	Hydrochloric acid
NaCl	Sodium chloride
NaOH	Sodium hydroxide
OM	Optical Microscope
PU	Polyurethane
WCA	Water Contact Angle
XRD	X-ray Diffraction

PNYEDIAAN DAN PENCIRIAN SALUTAN POLIURETANA HIDROFOBIK UNTUK PERMUKAAN KELULI

ABSTRAK

Permukaan hidrofobik adalah penolak kepada cecair berair dan media menghakis. Poliuretana (PU) mempunyai kehidrofobian yang boleh digunakan secara meluas dalam pelbagai bidang. Dalam projek ini, empat kaedah salutan berbeza iaitu tuangan jatuh, salutan putaran, salutan celup, dan salutan semburan digunakan untuk menghasilkan filem salutan PU hidrofobik pada 304 plat keluli. Di samping itu, nanoplatlet grafen (GNP) telah ditambah dalam PU dengan 0.5% (w/v) untuk meningkatkan sifat salutan PU manakala jaring keluli tahan karat 500 digunakan pada permukaan salutan untuk menghasilkan kekasaran permukaan salutan yang tinggi. Kemudian salutan dicirikan menggunakan FTIR, XRD, AFM, dan WCA serta ujian mekanikal seperti ujian tegangan dan ujian rintangan kakisan. Pengukuran salutan WCA selepas penambahan GNP ke dalam PU menunjukkan peningkatan kira-kira 12.04°-23.09°. GNP juga berjaya menurunkan kadar kakisan salutan dalam larutan NaCl 3.5% dengan menyekat ion menghakis daripada memasuki celah dan liang dalam PU. Kekuatan mekanikal filem meningkat dengan kehadiran ikatan hidrogen yang kuat dalam filem. Penggunaan jaring keluli tahan karat 500 telah meningkatkan kekasaran permukaan salutan dan juga membantu dalam meningkatkan WCA 5-8°, udara yang terperangkap di antara salutan dan persekitaran sekeliling melindungi permukaan salutan dengan tenaga permukaan yang rendah. Penggunaan jaring keluli tahan karat 500 boleh mengurangkan lagi kadar kakisan 304 keluli. Kajian ini menyediakan perbandingan menyeluruh morfologi permukaan salutan PU, PU-mesh, PU/GNP, dan PU/GNP-mesh, kehidrofobisian, dan rintangan kakisan.

ABSTRACT

Hydrophobic surfaces are repellent to aqueous liquids and corrosive media. Polyurethane (PU) has hydrophobicity which are widely applicable in various fields. In this project, four different coating methods which were drop casting, spin coating, dip coating, and spray coating used to fabricate hydrophobic PU coating films on 304 steel plates. In addition, graphene nanoplatelets (GNP) was added in PU with 0.5% (w/v) to increase the properties of PU coating while stainless-steel 500 mesh was applied on coating surface to create high surface roughness of coating. Then the coatings were characterized through FTIR, XRD, AFM, and WCA measurement as well as mechanical test such as tensile test and corrosion resistance test. The WCA measurement of coating after incorporation of GNP into PU showed the increasement about 12.04°-23.09°. GNP also successfully decreased the corrosion rate of coating in 3.5 % NaCl solution by blocking the corrosive ion from entering the gaps and pores in PU. The mechanical strength of film increased with the existence of strong hydrogen bond within the film. The application of stainless-steel 500 mesh improved the surface roughness of coatings also help in increasing the WCA of 5-8°, air trapped in between coating and surrounding environment protect the coating surface with low surface energy. The application of stainless-steel 500 mesh can further decrease the corrosion rate of 304 steel. This study provides a comprehensive comparison of PU, PU-mesh, PU/GNP, and PU/GNP-mesh coatings surface morphologies, hydrophobicity, and corrosion resistance properties.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Steels have widely used in many applications field because of its high tensile strength properties, cheap cost in fabrication including its high availability in multiple fields. It mostly performs in automobiles, ships building, machines, bridge, buildings, tools, and infrastructures. However, steel performance is limited when encounter dirt, oil, water, and harsh environment. Any material contained iron such as steel will corrode when in contact with air and water, thus steel needs to be kept dry condition, clean and avoid exposure to harsh environments. (Zhu & Wu, 2020).

Corrosion of metals causes large economic loss every year in the world. This explained why corrosion protection is needed especially in the field of pipeline, automobiles, marine, and construction. To protect steel from corrosion and any harsh environmental conditions, hydrophobic coating is suggested to act as protective layer of steel through coating techniques. Coating is one of the most effective techniques for protection of metallic components as coating can improve mechanical properties and corrosion resistance, the inspiration of hydrophobic coating came from plants and animals like butterfly wings, sharks' scales, and lotus leaves (Meena et al., 2020). Polyurethane (PU) is a synthetic polymer which can be used to provide the structural enhancement, optimum indoor temperature, and protection against harsh environment. Surface performance of steel surfaces can be enhanced through polyurethane coating. PU coatings provide flexibility, thermal stability, and inert to water, and chemicals. Metal and inorganic fillers are added into PU to fabricate modified PU coatings for advanced improvement of physical and chemical properties, in order to withstand harsh environment and able to perform at various requirements.

1.1.1 Fabrication techniques of Hydrophobic Polyurethane Coating

Generally, the techniques for synthesis hydrophobic coating are inspired by nature. Low surface energy and high surface roughness of a coating is desired to achieve hydrophobic coating. It can be concluded that hydrophobic coating can be achieved by either lower the surface energy or increase surface roughness of material or both. In this study, there are several coating techniques employed onto a substrate have been proposed below.

1.1.1(a) Drop casting

Drop casting is a versatile and easy coating technique used to fabricate a coating film on a substrate. In this method, polymer is dissolved into volatile solvent to obtain homogenous solution with low viscosity. The solution is applied on substrate surface by drop then followed by evaporation of solvent without any external work such as mechanical or thermal stress. This method leads to good distribution and regular arrangement of coating, as well as coating film with uniform thickness. A variety of additives options can be added into the polymer-solvent solution, which provide high possibilities to synthesis more advanced functional coatings in various application fields.

1.1.1(b) Spin coating

Spin coating is simple and versatile method for synthesizing a continuous coating film on substrate surface. Spin-coating process begins with the preparation of coating solution, the solution prepared is dispensed on central of the substrate surface subsequently, then the substrate is spun at a desired rotational speed. The steel plate spins around at the center which is perpendicular to the coating area during spinning process. Dispersed coating solution spreads until it reached the steel plate edge, forming a thin coating film on the substrate. The thickness of the coating film is influenced by the rotational speed, surface tension, and viscosity of the coating solution. Excess solvent is evaporated during the spinning process. Spined coating will form a relatively planar coating surface.

1.1.1(c) Spray coating

Spray coating is a technique spray aqueous or molten material onto a substrate surface by air pressure to produce a coating film. Spray coating method is a simple technique form coating on flat and irregularly surface product, it can be applied in continuous and large-area processing. The main benefits of this technique are the use of inexpensive materials, and it is a simple manufacturing process. Thus, it is mostly implemented in the fabrication of different types of coatings such as hydrophobic or hierarchical coatings on a wide range of substrates. Spraying method is the preferred method used to fabricate hydrophobic coatings which likely to incorporate with filler or with functionalized and low surface energy compound. This technique is also very useful in the case of metal substrates, as it is applicable to complex shape of substrate without any requirement before spraying such as pre-roughening step. The advantage of spray coating is its ability to provide coating films thickness at the range between 15 μm to a few mm with large surface areas.

1.1.1(d) Dip coating

Dip coating can create a uniform and thin coating onto cylindrical or flat shaped substrate. During dipping process, the substate is immersed in the low viscosity coating solution and then slowly removed and left for a few seconds on top of the tank to allow the removal and drainage of excess coating liquid, a homogeneous liquid film is formed on the substrate's surface. The solvent evaporated and formed thin coating film after drying at room temperature. Dip coating is suitable for to form coating on complex shapes and curved parts, which might not able coated by any technique. The advantage of the process is that no stress during the synthesis and no damage or distortion to the coating surface. Table 1 showing the advantages and disadvantages of several techniques of fabrication SHC are shown in Table 1.1 (Meena et al., 2020) (Anon, 2022).

Table 1.1 Advantages and disadvantages of fabrication techniques of SHC (Meena et al., 2020) (Anon, 2022)

Fabrication method	Advantage	Disadvantage
Drop casting	• Easy fabricate • Solvent of coating dried without external factors	• Highly dependent on solvent volatility • Requires high energy and high cost
Spin coating	• Quick drying • Controllable thickness	• Provides a smooth surface • Only for laboratory scale • Large amount of solvent is needed
Spray coating	• High quality coating • Repairable	• Requires more capital • Non-uniform thickness
Dip coating	• Industrially feasible • Reusable • Low cost	• Only for soluble polymers • Requires more time

1.2 Problem Statement

Hydrophobic polyurethane (PU) coatings can act as excellent barrier to steel and improve the lifetime of substrate as PU possesses to its excellent mechanical properties such as strong adhesion and good resistant. However, the lifetime of polyurethane becomes shorter due to the presence corrosive medium which can be found in nature such as acid rain or seawater. The chloride ion caused the degradation of PU chains. The defects of PU can be enhanced by advanced coating method or incorporation of filler into PU matrix. There are multiple designs and developments of improved properties of PU composite coatings and the enhancement of the existed composite may bring benefits in cost reducing and multiple fields. For example, waterborne polyurethane/reduced graphene oxide nanocomposite films were created by Li et al. (2016). The relationship between the nanofiller's dispersion state, chemical state, and the coatings' anticorrosive characteristics was investigated. When compared to the neat PU coating, anticorrosive capabilities of nanocomposite coatings were shown to be improved. (Li et al., 2016). In addition, selection of suitable coating method can greatly enhance the final coating properties. The polyurethane nanocomposite coatings must possess higher hydrophobicity property and high corrosion resistance in order to strengthen the lifetime of both PU and coated substrate. Thus, multiple studied of nanofiller such as Pb, Ni, Ag and Al incorporate in polyurethane which might reinforce the nanocomposite structure and properties, also can reveal their potential for UV protection, antimicrobial and corrosion resistance applications. (Kausar, 2018). In this study, graphene nanoplatelets are applied on the hydrophobic polyurethane coating and fabrication of hydrophobic coating on steel was conducted using different techniques.

1.3 Research Objectives

The aims of this project are:

1. To develop hydrophobic polyurethane (PU) coating on stainless-steel substrate using different techniques (drop casting, spin coating, spray coating, and dip coating)
2. To investigate the effect of GNP addition on the surface morphology, water contact angle, corrosion resistance and tensile properties of coating.
3. To evaluate the effect of stainless-steel mesh applied on the surface morphology, surface roughness, water contact angle and corrosion resistance of Pu and PU/GNP coatings.

1.4 Thesis Outline

This research aims to employ four different coating methods which are drop casting, spin coating, spray coating, and dip coating to synthesize hydrophobic polyurethane coating. Graphene nanoplatelets reinforced polyurethane aims to improve the polyurethane-based coating properties such as hydrophobicity, tensile strength, and corrosion resistance. Besides, the amount of coating solution coated on steel surface was varied to determine their effect towards the final properties of PU/GNP coating. The samples produced will undergo various characterizations such as Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Tabletop-Scanning Electron Microscope (SEM), Water Contact Angle (WCA) measurement, Atomic Force Microscopy (AFM), Tensile test, and corrosion resistance test.

1.5 Thesis Outline

This thesis involves 5 chapters.

Chapter 1 covers introduction part including the research background, problem statement, research objectives and scope of research.

Chapter 2 covers the literature review on the hydrophobicity, Young's equation, Wenzel model, Cassie-Baxter model, polymer composite coating, polyurethane, isocyanates, polyols, other materials used for polyurethane such as catalysts and chain extenders, polyurethane/nanocomposite coating, polyurethane/graphene derived nanofiller-based coating, polyurethane/graphene nanoplatelets filler coating, and applications of hydrophobic surfaces.

Chapter 3 describes the materials, experimental methodology, parameters, and characterization methods utilised in this project.

Chapter 4 presents the results and discussion of the research.

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

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrophobicity

A hydrophobic surface is known as the surface with water contact angle (WCA) more than 90°. A water droplet slides off from the hydrophobic surface easily, also allow dirt washes off and cleaning the surface effectively. The inspiration of hydrophobic coating came from natural animals like shark's scales, butterfly wings, pond skater, gecko foot, and lotus eaves (Meena et al., 2020). This phenomenon is known as self-cleaning. Hydrophobic properties are highly demand for numerous applications, including impermeable textiles and coatings. Hydrophobic surfaces have anti-sticking and anti-contaminating properties which able to repel dirt and water, so that the surface can remain inert to air and moisture for comfort. Low surface energy materials and high surface roughness are desired to synthesis a hydrophobic surface. Wettability is an important aspect of hydrophobic coating as the degree of hydrophobic surface depends on the surface wettability characteristic of that surface. In wetting research, the contact angle reveals the amount of wetting value there is when a liquid and solid come into contact. Figure 2.1 illustrates the formation of the water contact angle when a liquid drop is put on the surface. A large contact angle results from a smaller area of contact between the liquid and the solid (Yuan & Lee, 2013).

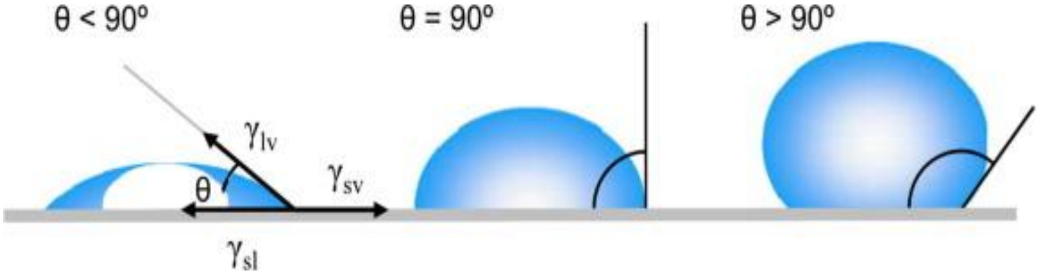


Figure 2.1 Water contact angles formed by liquid drops on a smooth homogeneous solid surface (Yuan & Lee, 2013)

Wettability is affected by the surface energy and surface roughness. Decrease in surface energy and uneven surface are imperative to achieve the hydrophobic property. Surface energy can be lowered by adding surfactant in the coating. Surfactants diffuse in the coating solution and absorb at the air and coating solution interfaces. The hydrophobic group may move out of the bulk water phase, heading into the air while water soluble hydrophilic group remains in the water or coating solution. Thus, water drop found on hydrophobic surface will have small contact angle between solid and liquid (Bera et al., 2018). Surfactant monomer representing the hydrophilic head and hydrophobic tail is shown in Figure 2.2.

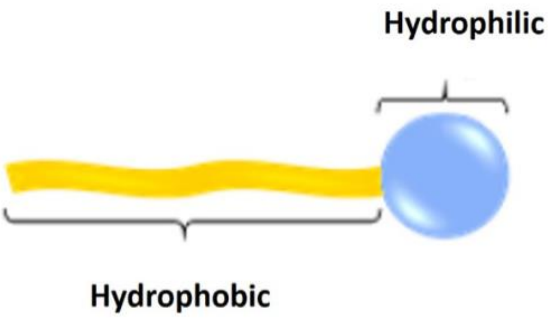


Figure 2.2 Surfactant monomer representing the hydrophilic head and hydrophobic tail (Raeisi et al., 2021)

Rough surfaces can trap air in their voids, reducing the surface area in contact between the coating and the steel. Air bubbles trapped in between surface’s peaks and valleys after a liquid drop is placed on the coatings surface, preventing the liquid drop from making full contact with the surface. The valley's low surface energy and the abundance of air prevent water from penetrating it.

As a result, the surface area is lowered, which lowers friction. Droplets thus glide across the surface with ease. Three major wetting theoretical models’ equation, Young's Wenzel mode, and Cassie-Baxter model have been used during the past few decades to study the wettability of solid surfaces and the physical interactions between solids and liquids. Each model's basic tenets are presented. Figure 2.3 illustrates the Young's equation, Wenzel mode, and Cassie-Baxter models as wetting theoretical models.

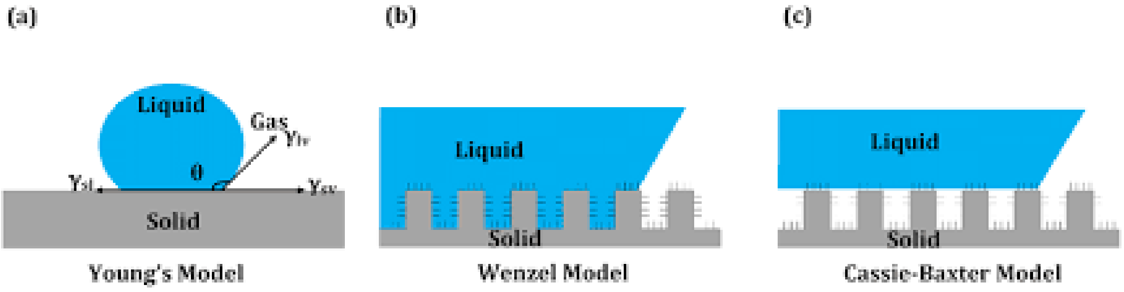


Figure 2.3 Wetting theoretical models of (a) Young’s equation; (b) Wenzel mode; (c) Cassie-Baxter model (Samanta et al., 2020)

2.1.1 Young’s equation

In 1805, Young's equation, the first model, was presented. The solvent surrounding the contact solid surface is assumed in this model to be inert to one another. This model calculates the static contact angle of a fluid drop on a perfect solid surface that is smooth, insoluble, homogenous, and rigid. Young’s equation elaborates wetting by the surface free energy of a solid and derived by equation (1). Only the contact angle produced by the free energy surfaces' thermodynamic equilibrium at the solid-liquid-gas interface is described by Young's equation.

$$\cos\theta_c = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

Where, θ = contact angle, γ_{SV} = surface tension of the solid-vapor interface, γ_{SL} = surface tension of the solid-liquid interfaces, and γ_{LV} = surface tension of the liquid-vapor interfaces. The equation shows a direct link between the surface energy and contact angle. Young's equation, however, cannot explain most contact angle states because real surfaces often feature a variety of surface conditions and surface roughness of solids that affect wettability.

2.1.2 Wenzel model

Young's equation concept was updated to create the Wenzel model. It is designed to specify if a homogeneous rough surface is wettable. In 1936, the Wenzel model equation demonstrated that the surface energy and roughness are related to the contact angle according to equation (2):

$$\cos\theta_c = \mathrm{r}\cos\theta_c = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \tag{2}$$

Where, θc = Contact angel influenced by surface roughness and r = roughness factor. The ratio of the real surface to the geometric or planar surface can be thought of as the roughness factor, as illustrated in equation (3). As a result, a surface that has been roughened will always show a number higher than 1.

$$r = \frac{Actual\ Surface}{Geometric\ project\ surface} \tag{3}$$

Wenzel model assumed that the contact between solid surface and liquid for homogenous wetting are fully close with each other. Wenzel model defines the wettability of surface through the energy different made by the dried surface and wetted surface. Surface roughness can alter the wettability and anti-wettability, the contact angle increased when surface roughness increased. The surface energy of a substant depends to its surface chemistry, which means that existing of interface formed by the energy change on the surface will affect

Due to the increased contact area, when a surface is roughened, the surface energy of a specific unit area increases in accordance with the surface's intrinsic wettability. It should be noted that since a solid's specific surface energy depends on its surface chemistry, it remains unaltered. On the rough surface, however, the energy change brought on by the creation or destruction of a new interface will be more pronounced. According to one theory, surface wettability and roughness are inversely connected, so a surface that is getting more hydrophobic will allow for corresponding increases in contact angle. In contrast, an innately hydrophilic substance will experience the reverse result because its contact angle tends to be zero.

2.1.3 Cassie-Baxter model

In 1944, Cassie-Baxter was developed to offer an additional model for situations in which a liquid droplet encounters a homogeneous or heterogeneous solid surface. They have two components to their model. Surface fraction, f1, and contact angle, 1, are included in the first section, and f2 and 2 are included in the second part. Hence, in Cassie-Baxter's equation, the contact angle is defined as equation (4):

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{4}$$

where θ is the contact angle in the model of Cassie-Baxter and fi is the surface area fraction with contact angle θ_i ($f_1 + f_2 = 1$). The model of Cassie-Baxter makes the assumptions that air pockets are confined beneath the liquid and that the liquid only comes into contact with the solid at the roughness tips. In this situation, it can be regarded as a region on the surface where air is trapped rather than wetted by liquid. The θ_2 will be

180° if there is only air between a solid and a liquid. Therefore, equation (5) can be written as followed equation:

$$\cos\theta_{CB} = f_s\,(\cos\theta_s + 1) - 1 \tag{5}$$

where fs is the solid surface fraction with a contact angle of θs. In addition to the models listed, more improved models have been provided in references to predict the specific modes of wetting.

Another significant aspect that explains the use of super-hydrophobic roughness to increase the corrosion resistance of metals is capillarity. The height (h) of the water column inside the tube can be determined by the equation (6):

$$\mathrm{h} = \frac{2\gamma\cos\theta}{\rho g R} \tag{6}$$

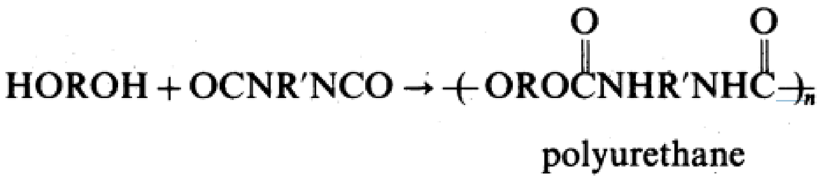
where γ is the surface tension, θ is the contact angle, ρ is the liquid density, g is the gravity acceleration and R is the cylindrical tube radius. A vertical cylindrical tube poured into a liquid is thought of as a hydrophobic surface. The hydrophobic surface has exceptionally small pores and a water contact angle value of 150°. As a result, the hydrophobic surface's pores can be entirely sealed off by the Laplace pressure, preserving the substrate from corrosion in the harsh environment.

2.2 Polymer composite coating

Polymer coatings can be applied to complex structure surface, they are used to act as corrosion protection and decorative layers. In recent year, development of polymer coating incorporated with nanoparticle has been introduced in the manufacturing of high-performance coating systems. Although polymer coatings are, but they can incorporate with inorganic nanoparticle to improve properties including aesthetics and functionality. The durability of polymer coating can be also extended by incorporation of nanomaterials in it. The common nanofiller or nanoparticle added into polymer coating such as zinc sulfide (ZnS), zinc oxide (ZnO), titania (TiO_2), alumina (Al_2O_3), and silica (SiO_2) (Ching et al., 2018). With the incorporation of nanoparticle in polymer solution, they can be formulated according to the specifications required by processing site, and tunable to fabricate desired coating thickness and properties. The fabrication cost of the polymer coating can be reduced as well as the fabrication time.

2.3 Polyurethane

Polyurethane (PU) unique property allow they become an attractive material at wide range of applications such as automotive part, water proofing membranes, electronic potting, and encapsulation, etc. The property of PU depends to the compositions of hard and soft segments, chain extender and additives used. They able to offer rubber elasticity combined with toughness and durability of plastic because of their property. The segmented polyurethane has various disperse blocks of hard and soft segments in alternate manner. Polyurethane can be produced by various methods, the most widely used fabrication technique is the reaction of di- or poly-functional isocyanates with di- or poly-functional hydroxy compounds (polyol), with the addition of a chain extender, catalyst, or other additives. The fabrication of polyurethanes through the polyaddition procedure is shown in Figure 2.4.



$$\mathrm{HOROH} + \mathrm{OCNR'NCO} \rightarrow \underset{\text{polyurethane}}{\left(\mathrm{ORO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHR'NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right)_n}$$

Figure 2.4 Synthesis of polyurethanes (Zafar, 2012)

2.3.1 Isocyanates

Isocyanates are the most reactive components of polyurethane. It is the essential component needed for fabrication of PU. These are di-or polyfunctional isocyanates contain highly reactive isocyanate groups (–N=C=O)/(NCO) and have two accumulative double bonds. Isocyanates also have mesomeric structures presented as –N(δ–) –C(δ+) –O(δ–), this structure results the reaction possibility of isocyanate group with hydroxyl groups. Their highly reactivity toward hydroxyl groups allows highly efficient during polyurethane production. Isocyanates are category into several types, they can be aromatic, polycyclic, cycloaliphatic, or aliphatic in nature. Figure 2.5 shows examples of some common isocyanates such as hexamethylene diisocyanate (HDI), methylene dipheneyl diisocyanate (MDI), Toluene diisocyanate (TDI), 1,5-naphthalene diisocyanate (NDI), 4,4’-methylene bis (cyclohexyl isocyanate), and 1,6 isophorone diisocyanate (IPDI).

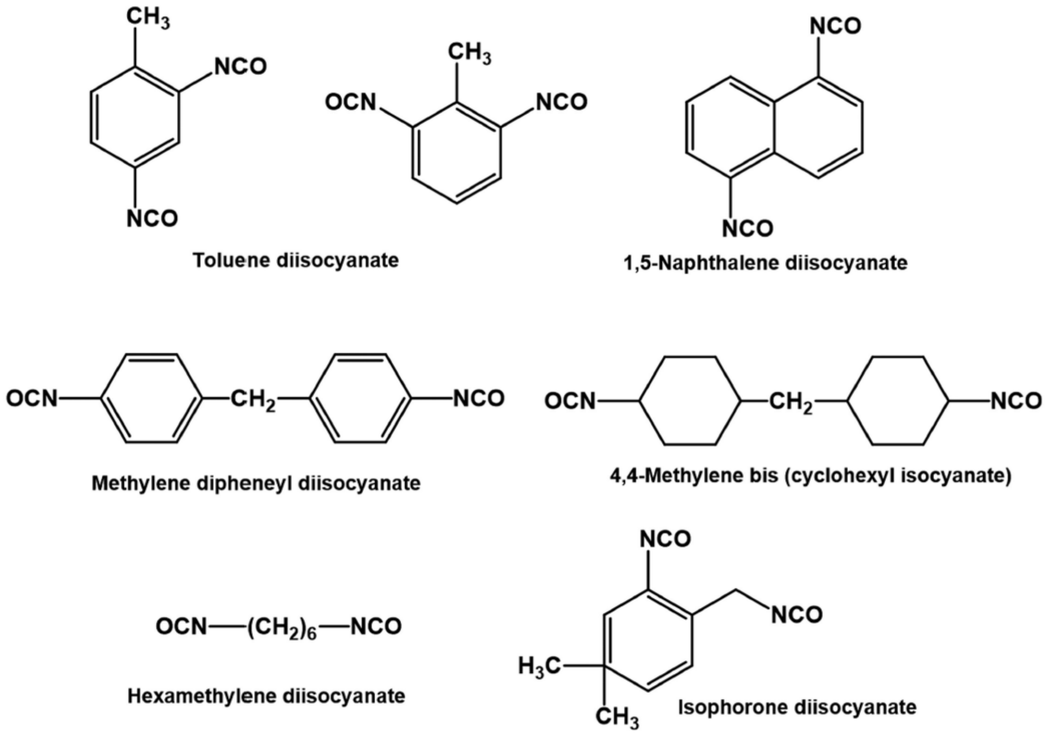


Figure 2.5 Common isocyanates for polyurethanes (de Souza et al., 2021)

Aromatic isocyanates are widely used as it is less toxic, more reactive, lower oxidative and more ultraviolet stabilities. Aromatic isocyanates having double bond sequence, R-N=C=O, wherein the reactivity of isocyanate is governed by the positive charge of the carbon atom (Figure 2.6), which is more likely to get attacked by nucleophiles, nitrogen and oxygen by electrophiles. The negative charge gets delocalized into aromatic group. (Figure 2.7) This indicate that cycloaliphatic or aliphatic isocyanates are less reactive compared to aromatic isocyanates (Zafar, 2012).

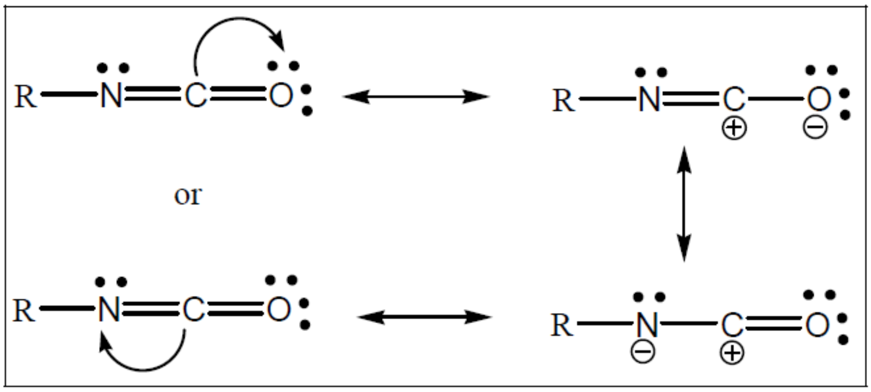


Figure 2.6 Resonance in isocyanate (Zafar, 2012)

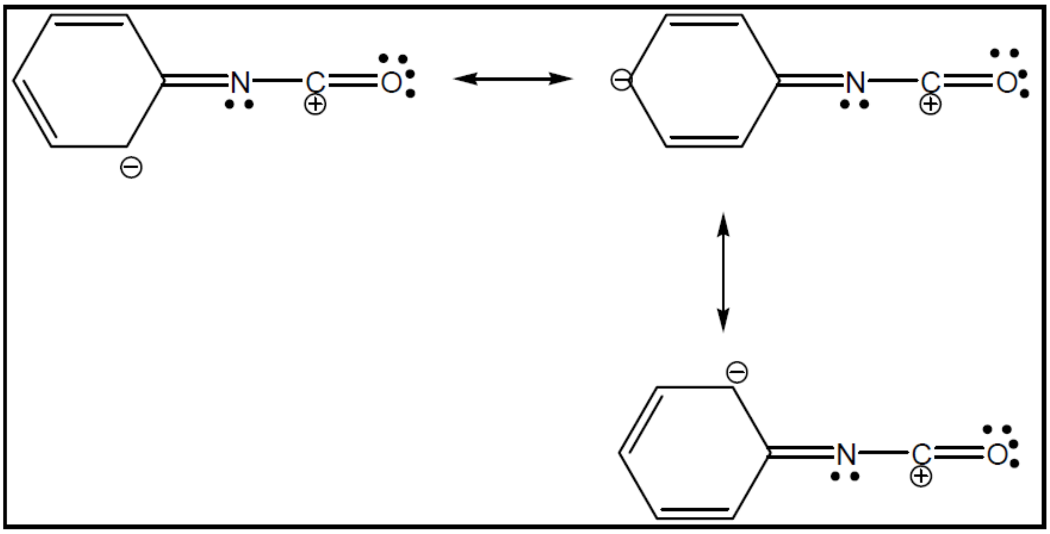


Figure 2.7 Resonance in aromatic isocyanate (Zafar, 2012)

The characteristics of PU are affected by the rigid segments that aromatic isocyanates add to the PU structures. For instance, as they contain aromatic structures, methylene diphenyl diisocyanate and toluene diisocyanate (TDI) are focused on for the fabrication of thermoset polyurethanes. They are the favored isocyanates for industrial applications because they are more affordable than other isocyanates and have higher reactivity. But when exposed to UV light, aromatic isocyanates have a tendency to turn yellow or brown because of their limited UV light stability. As a result, they are frequently employed for indoor purposes. (de Souza et al., 2021). Toluene diisocyanate

(TDI), methylene diphenyl diisocyanate (MDI), and 1,5-naphthalene diisocyanate are examples of aromatic isocyanates (NDI). Since aliphatic isocyanates mix well with pigments, they are more frequently utilised in coating applications. Aliphatic isocyanates are used to create PU coatings that are UV stable and maintain gloss. Isocyanate-terminated polyurethanes are typically hydrophobic, stiffer, and chemically stable. (de Souza et al., 2021). Hexamethylene diisocyanate (HMDI) and isophorone diisocyanate are two examples of aliphatic isocyanates (IPDI).

2.3.2 Polyols

Polyols are materials that bearing plurality of hydroxyl groups, the hydroxyl (OH) groups from polyols will react with isocyanate (NCO) groups from isocyanates to synthesis polyurethane. Polyester polyols (PEP) and polyether polyols (PETP) are two common types of polyols. Generally, they are made through a condensation process between glycols. 1,6-hexanediol, 1,4-butanediol, ethylene glycol, and a dicarboxylic acid/anhydride (aliphatic or aromatic). The molecular weight of the polyol utilised determines how much of the PU is cross-linked. Meanwhile high molecular weight long chain polyols offer good flexibility to PU but poor chemical resistance, low molecular weight polyols produce rigid PU with high heat and chemical resistance. (Zafar, 2012). Figure 2.8 provided examples of polyols along with their functionality. The most common polyols utilised for the production of flexible polyurethanes are polyether polyols. They can be made by adding ethylene or propylene oxide to starters or initiators that are alcohol or amines with the help of an acid or base catalyst. High moisture permeability and a low glass transition temperature (Tg) in polyether-based polyurethanes prevent them from being widely used in coatings and paints. Plus, PETP is less expensive than PEP. Poly (tetramethylene ether) glycol, polyethylene glycol (PEG), and polypropylene glycol (PPG) are examples of polyether polyols (PTMG).

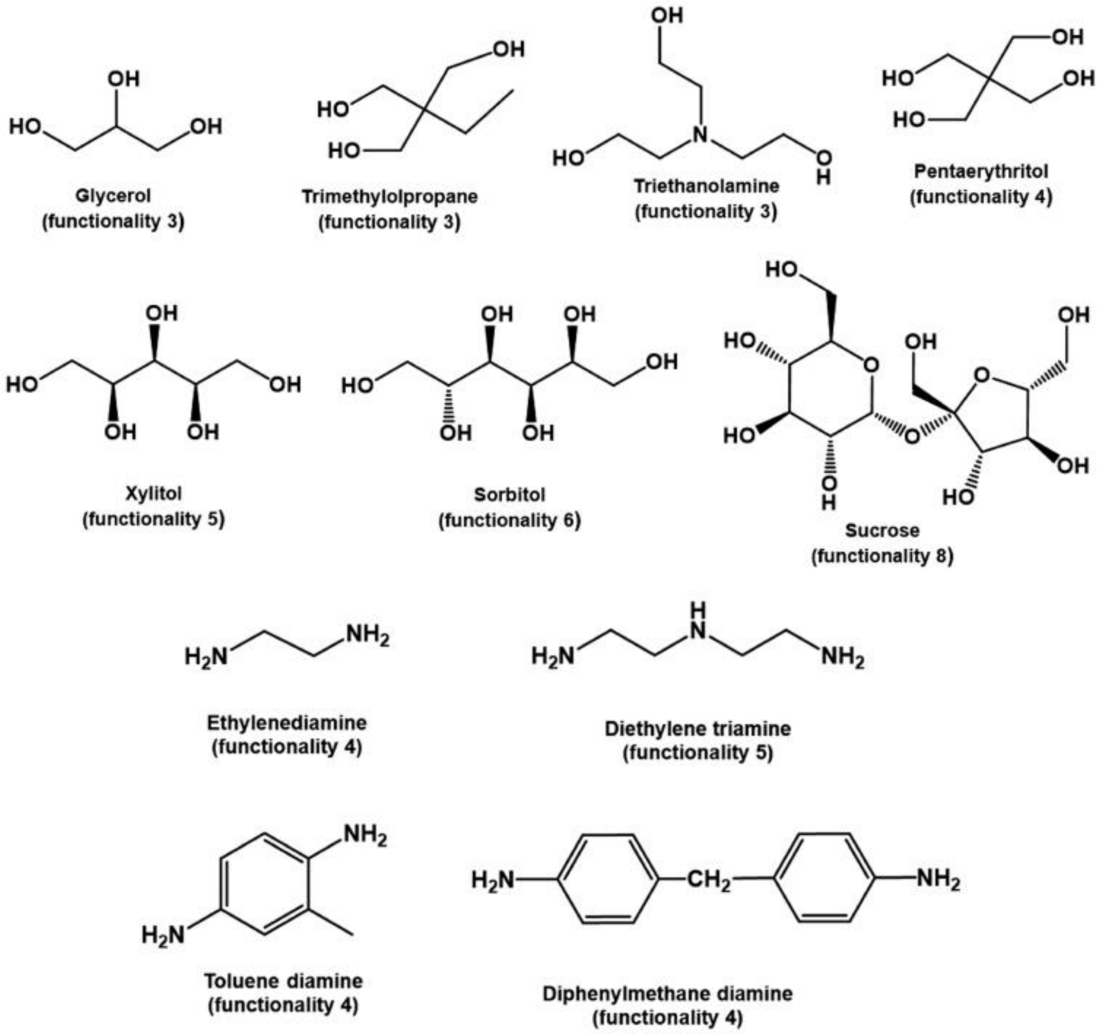


Figure 2.8 Examples of some starter polyols along with their functionality (de Souza et al., 2021)

The second most common polyol used in the manufacture of polyurethanes is polyester polyol. In comparison to polyether-based polyurethanes, PU made from PEP has qualities like better crystallinity because of stronger intermolecular connections between polymeric chains, higher thermal stability, and enhanced fire resistance. When subjected to heat and moisture for an extended period of time, they may also experience hydrolysis. They can be created either by a ring-opening reaction involving cyclic carbonates or lactones or by a polycondensation reaction involving polyols and multifunctional carboxylic acids. (de Souza et al., 2021). The reaction can be self-catalyzed since carboxylic acid groups are acidic. Polycaprolactone (PCL) diol and polyethylene adipate (PEA) diol are two examples of polyester polyols.

2.3.3 Other Materials used for Polyurethanes

The primary ingredients used in the synthesis of polyurethanes are isocyanates and polyols. The characteristics of polyurethanes are determined by the chemical makeup and functions of polyols and isocyanates. The shape, porosity, density, mechanical strength, and rate of reaction are only a few examples of the attributes that can be impacted by additional ingredients utilised in the synthesis of polyurethanes. Materials including surfactants, chain extenders, catalysts, cross-linkers, and blowing agents have an impact on the characteristics of PU.

2.3.3(a) Catalysts

Catalysts are substances that can change a reaction's activation energy and so regulate the rate at which PU product is produced. By enhancing production efficiency, enabling quicker manufacture, and speeding up curing procedures, they can significantly boost the economic benefits of manufacturing facilities. (de Souza et al., 2021). Catalysts with the ability to regulate the relative reaction speed can change the structure and characteristics of the final PU product. Catalysts commonly used are tertiary amine-based catalysts such as dimethylcyclohexylamine, dimethylethanolamine, triethylenediamine, and 1,4-diazabicyclo [2.2.2] octane. Figure 2.9 showed the chemical structures of catalysts.

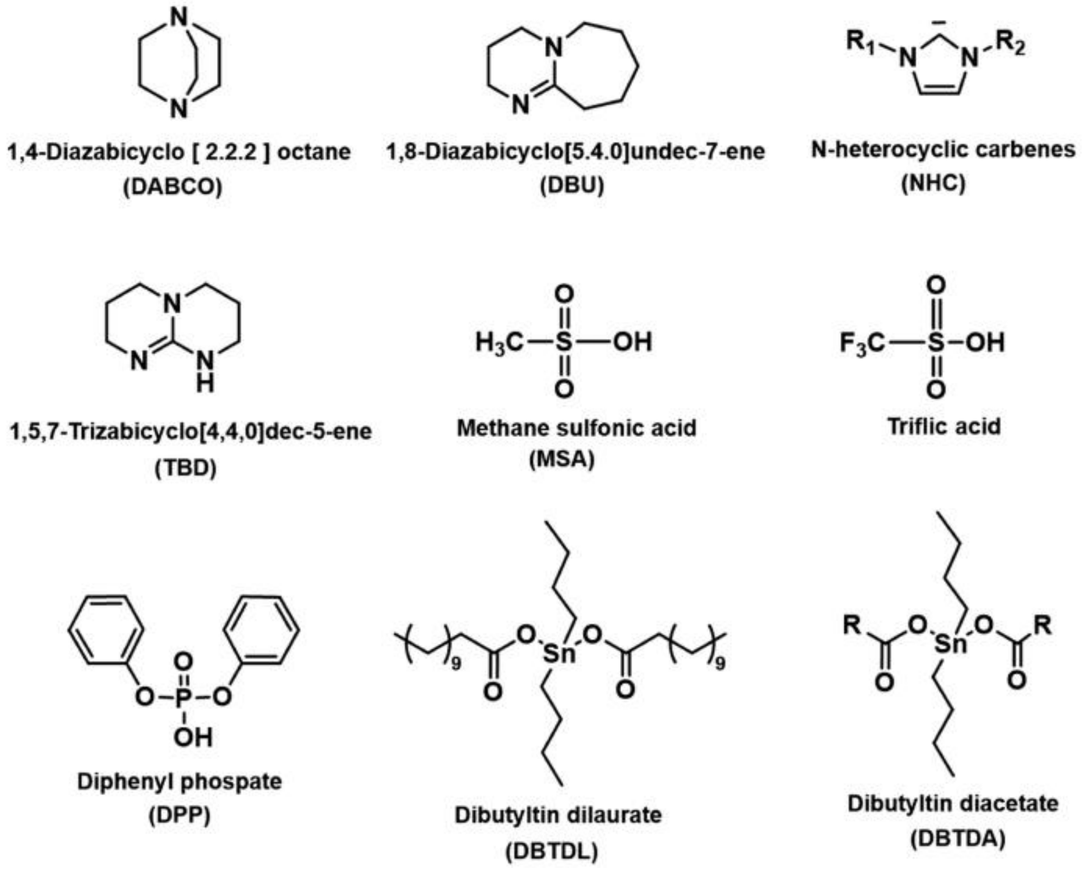


Figure 2.9 Most employed catalysts for the synthesis of polyurethanes (de Souza et al., 2021)

2.3.3(b) Chain Extenders

Chain extenders are, difunctional molecules with typically low molecular weight. Chain extenders can be divided into three groups: hydroxyl amines, diols, and diamines. It is included to act as a separator between nearby isocyanates. The shape, cellular structure, and thermal and mechanical properties of polyurethane are significantly influenced by chain extender structures. Chain extenders with a functionality of 2 can improve the rigidity of the isocyanate groups by introducing rigid domains through their short, low-mobility chains, but the elasticity of polyurethane also declines as a result. Higher functioning chain extenders form a covalent bond between the polymeric chains, a cross-linked structure, and a densely connected network. Due to the presence of chemical bonds rather than weaker intermolecular interactions, cross-linked polyurethane is mechanically stronger than the corresponding linear chain-based polyurethane. Additionally, cross-linking affects the thermal characteristics. At a temperature greater than their glass transition temperature, linear or thermoplastic polyurethane becomes liquid. However, strongly cross-linked polyurethanes (PU) breakdown rather than fluidize at higher temperatures. Thermoset polyurethanes are thermally stable due to the increased energy needed to break chemical bonds. Chain extenders are depicted in Figure 2.10 connecting isocyanates with urethane linkages (*Polyurethanes*, n.d.).

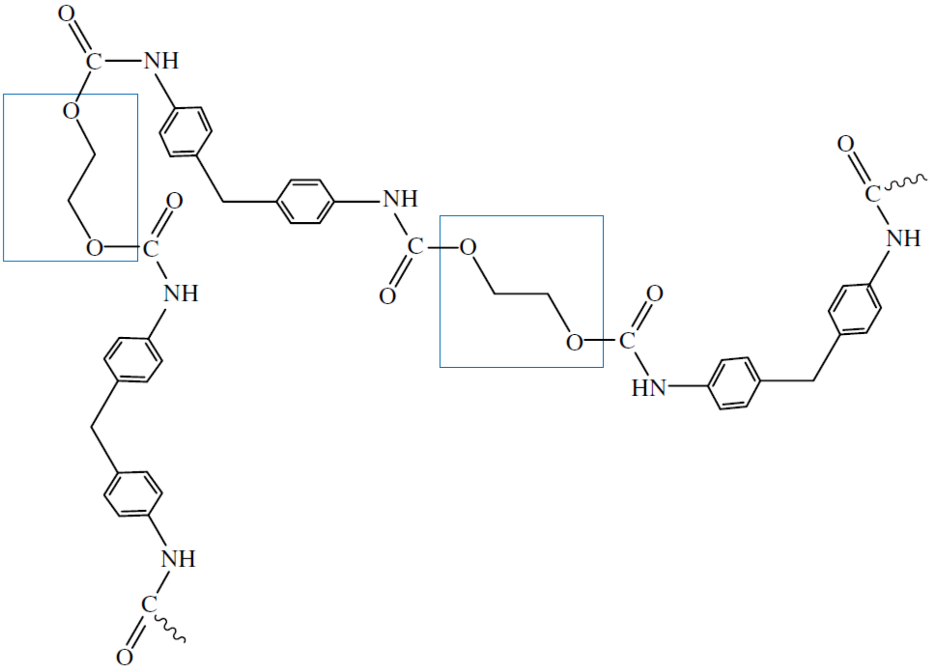


Figure 2.10 Chain extenders (in boxes) linking isocyanates through urethane bonds (*Polyurethanes*, n.d.)

2.4 Polyurethane/nanocomposite coating

The characteristics of a polymer composite can be significantly enhanced by adding nanoparticles to the matrix. It offers a fresh approach to polymer composite modification that is superior to the inclusion of microparticles. Through physical or chemical interaction, some nanoparticle surface properties offer higher interfacial adhesion and improve the network structure. The organic coatings have frequently been treated with carbon nanoparticles. According to research, polyurethane and inorganic nanoparticle coatings hold potential for applications in antimicrobial activity, UV protection, friction, wear, and corrosion resistance. However, there are a number of undiscovered inorganic nanoparticle kinds that can be added to PU coatings to provide great performance for cutting-edge applications. Excellent weather resistance, electrical qualities, abrasion resistance, and moisture or solvent resistance may all be characteristics of polyurethane coatings and adhesives.

A modified silicon dioxide/polyurethane (IEM-SiO2/Si-PU) superhydrophobic coating with excellent performance with a water contact angle of 160° and sliding angle of 2° was successfully produced by Hus Liu et al through spray coating and cured under UV lamp for 3 minutes (Liu et al., 2020). When applied to a variety of surfaces, including plastic, paper, aluminium, and glass, the coating exhibits superhydrophobic properties. The coating has outstanding mechanical qualities as well. After 400 cycles of friction, it still has a 150° water contact angle, and 100 minutes of ultrasonic vibration doesn't change its superhydrophobic properties. WCA would not affected much as the silica nanoparticles anchored on the resin layer have a strong resistance to abrasion. The coating, which is extremely hydrophobic to both acidic and alkaline environments, maintained good durability and hydrophobic performance after soaking for 24 hours in a pH environment ranging from 1 to 14. Additionally, the application range of this durable