Crossref DOI: 10.31643/2024/6445.36 Engineering and Technology

© creative

# Polyurethane as a versatile polymer for coating and anti-corrosion applications: A review

<sup>1\*</sup>Yeligbayeva G., <sup>2</sup>Khaldun M. A., <sup>3</sup>Abdassalam A. Alfergani, <sup>4</sup>Tleugaliyeva Zh., <sup>4</sup>Karabayeva A., <sup>1,5</sup>Bekbayeva L., <sup>6</sup>Zhetpisbay D.S., <sup>7</sup>Shadin N.A., <sup>1</sup>Atabekova Z.

<sup>1</sup>School of Petroleum Engineering, Satbayev University, Almaty, Kazakhstan

<sup>2</sup>Department of Chemistry, School of Science, The University of Jordan, 11942, Amman, Jordan

<sup>3</sup>Chemistry Department, Faculty of Education, Sirte University, Sirte, Libya

<sup>4</sup>School of Materials Science and Green Technologies, Kazakh-British Technical University, Almaty, Kazakhstan.

<sup>5</sup>National Nanotechnology Open Laboratory, Al-Faraby Kazakh National University, Almaty, Republic of Kazakhstan

<sup>6</sup>Department of Biochemistry, School of General Medicine-1, S.D. Asfendiyarov KazNMU, Almaty, Kazakhstan

<sup>7</sup>Department of Chemistry, Institute of Natural Sciences and Geography, Abai Kazakh National Pedagogical University, Almaty, Kazakhstan

\*Corresponding author e-mail: g.yeligbayeva@satbayev.university

#### ABSTRACT

Received: <i>November 23, 2023</i> Peer-reviewed: <i>December 8, 2023</i> Accepted: <i>December 15, 2023</i>	The development of polyurethane materials and process optimization are currently the subjects of extensive study. Polyurethane is characterized by high physicochemical and operational properties. Polyurethanes have high wear resistance, and oil and gasoline resistance. They have excellent thermophysical and elastic properties. This allows the use of polyurethanes in many industries where materials with high-performance properties are required. Polyurethanes are widely used in many industrial applications, protective coating manufacturing, and anti-corrosion agent applications. A significant number of studies have been conducted to improve the physical, mechanical, and operational properties of polyurethane polymers, in particular the anti-corrosion properties of modified polyurethane coatings. The properties of polyurethane polymers for various applications can be improved by changing monomers and their ratios and the process of preparations. Preparation of polyurethane polymers based on polyols and isocyanate monomers using a polyaddition process in the presence of a catalyst as well as solvents including toluene, xylene, and acetone. There are different factors affecting the physical and mechanical properties of polyurethane polymers were investigated by different techniques. The factors were types of isocyanates, polyols, OCN/OH ratios, solvents, catalysts, and temperatures. Generally, the polyols are responsible for the flexibility of the polyurethane polymer and crosslinking between the backbone of the polymer. Because of the flexibility of its chemistry, they may modify the coating's characteristics based on the intended use. The effects of different polyols and polyisocyanates' chemistry are assessed. The hydrophobicity, thermal stability, and mechanical and anti-corrosion properties of polyurethane polymers were investigated. As a result, the properties of polyurethane polymers such as hydrophobicity, thermal stability, and mechanical and anti-corrosion properties were all enhanced when all the above fa	
	given in this review article.	
	Keywords: Polyurethane, coating, anti-corrosion, polyols, polyisocyanates.	
Yeligbayeva Gulzhakhan Zhakparovna	School of Petroleum Engineering, Satbayev University, 22 Satpayev Street, 050013, Almaty, Kazakhstan. Email: g.yeligbayeva@satbayev.university	
Khaldun M. Al Azzam	Department of Chemistry, School of Science, The University of Jordan, 11942, Amman, Jordan. Email: azzamkha@yahoo.com	
Abdassalam A. Alfergani	Chemistry Department, Faculty of Education, Sirte University, Sirte, Libya. Email: abdassalamtameem@yahoo.com	
Tleugaliyeva Zhanetta Ashatovna	School of Materials Science and Green Technologies, Kazakh-British Technical University, 59 Tole bi Street, 050000, Almaty, Kazakhstan. Email: z_tleugalieva@kbtu.kz	
Karabayeva Aykumis Yermekkyzy	School of Materials Science and Green Technologies, Kazakh-British Technical University, 59 Tole bi Street, 050000, Almaty, Kazakhstan. Email: a_karabayeva@kbtu.kz	
Lyazzat Bekbayeva	National Nanotechnology Open Laboratory, Al-Faraby Kazakh National University, al-Farabi av., 050040, Almaty, Republic of Kazakhstan. Email: lyazzat_bk2019@mail.ru	
Zhetpisbay D.S.	Department of Biochemistry, School of General Medicine-1, S.D.Asfendiyarov KazNMU, 480012, Tole bi, 88, Almaty, Kazakhstan. Email: zhetpisbay.d@kaznmu.kz	
Shadin N.A.	Department of Chemistry, Institute of Natural Sciences and Geography, Abai Kazakh National Pedagogical University, 30 Kazybek Bi str., Almaty, Kazakhstan. Email: nugen_87@mail.ru	
Z.B. Atabekova	School of Petroleum Engineering, Satbayev University. Engineer. Email: zau888@mail.ru	

= 21 ====

### Introduction

Several years ago, the coating industry used various polymers to manufacture a wide range of coating goods such as acrylic, epoxy, alkyds, polyurea, and polyurethane. Polyurethane was created via polyaddition polymerization of several formulations containing isocyanates and polyols [[1], [2], [3]]. Additives were also applied by the method and product type. They were made without solvent using different isocyanate monomers such as aliphatic and aromatic, and different polyols such as polycarbonate, polyester, and polyether since their toxicity polluted the atmosphere and harmed the ozone layer.

The primary purpose of this review is to screen and adapt prepolymers based on aliphatic and aromatic polyurethane polymers for industrial coatings, particularly anti-corrosion coating. These prepolymers will be environmentally sustainable and have the greatest physical properties. The project will focus on the development of anticorrosion coatings based on polyurethane prepolymers, both aliphatic and aromatic. An

alternate isocyanate and hydroxyl ratio should be studied to produce the desired product. When combined with additives such as fillers, thickeners, plasticizers, and crosslinking agents, the product produces the appropriate anti-corrosion coatings for pipeline applications. The current study aimed to develop the technology and find the materials and polymers that play important roles to reduce or prevent the corrosion rate of metals.

### Polyurethane

Polyurethanes (Pus) are one-of-a-kind polymeric materials with a wide range of physical and chemical characteristics that have been employed in a variety of applications, including foams, coatings, adhesives, and thermoplastic elastomers [[3], [4], [5], [6], [7], [8]]. Material selection, polymer design, production conditions, and application procedures can all be used to create PUs. Polyurethane chemistry is based on isocyanate reactivity toward hydroxyl and amine groups. The isocyanate group's reactivity is attributed to the positive charge of the carbon atom in the N=C=O group's cumulated double-bond system, as seen in Figure 1.

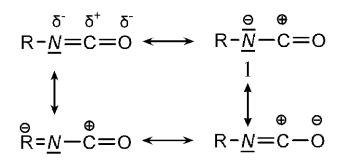


Figure 1 - Resonance structure of the isocyanate group

Isocyanates react with all molecules containing "active" hydrogen atoms, including water, hydroxyl, and amine groups, at temperatures ranging from 60 to 90 °C depending on catalyst type and concentration [9]. The exothermic, reversible process produces urethane. Polyurethane polymers or polyurethane-polyurea polymers containing both urethane and urea groups are used to make PUs, which are created by polyaddition reactions of polyols, polyisocyanates, and polyamines, as illustrated in Figure 2. Polyisocyanate is a molecule that has two or more isocyanate functional groups, while polyol contains two or more hydroxyl groups [10]. Because urea groups are known to interact via bifurcated hydrogen bonds, they are good functionality for usage in hard segments of thermoplastic elastomers. Compared to urethanes and amides, they have a stronger hydrogen bond. Poor melt processibility and insufficient solubility in organic solvents are two disadvantages of these elastomers, though. The temperatures at which urea segments melt or soften are significantly greater than their thermal breakdown temperatures due to the extremely strong bifurcate hydrogen bonding between urea groups.

As illustrated in Figure 3, more "active" hydrogen atoms are present in the urethane and urea groups that are produced, and these groups can react with isocyanate to produce allophanates and biurets.

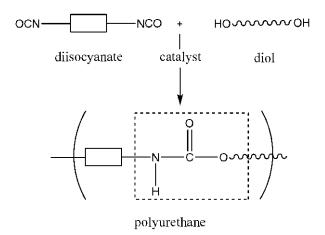


Figure 2 - Polyaddition reaction between diisocyanate and diol

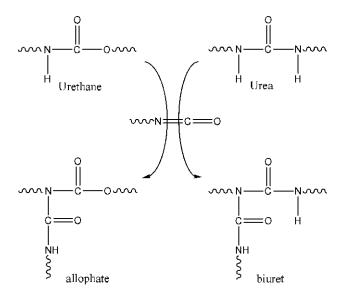


Figure 3 - Urethane and urea groups reacted with isocyanates

Polyols and additives like catalysts, cross-linkers, and polyisocyanates—which produce the polymer's hard segments—make up the raw ingredients for polyurethanes. The polymer's soft segments are inexorably formed by the transistor.

### Polyisocyanates

The primary products needed to create polyurethane polymers are isocyanates containing two or more functional groups [11]. PUs' cost and quality are determined by the kind of diisocyanates used, such as aliphatic and aromatic dimethyl cyanide. The bulk of diisocyanates produced worldwide are aromatic isocyanates, despite their low UV resistance. However, because of their strong UV resistance, aliphatic and cycloaliphatic isocyanates are also crucial for the production of polyurethane materials for outdoor applications. Aliphatic isocyanates are strongly advised. This is because the reactivity of an isocyanate group with an aromatic connection is much higher than that of an aliphatic one. The lower cost of aromatic isocyanates compared to aliphatic isocyanates is another consideration. Isocyanates are distinguished by the percentage of NCO content and their functionality, which reflects the number of NCO groups present in a molecule. Table 1 lists the most regularly utilized isocyanates in the manufacturing of polyurethanes.

The authors studied the properties of segmented PU produced from various diisocyanates [12]. Using 4,4'-diphenylmethane diisocyanate (MDI), 2,4-toluene diisocyanate (TDI) and its isomers, hydrogenated 4,4'-diphenylmethane diisocyanate (HMDI), and 1,6-hexane diisocyanate

\_\_\_\_\_ 23 \_\_\_\_\_

No.	Chemical name	Abbreviation	Structure
1	toluene -2,4 -diisocyanate	TDI	CH3 NCO NCO
2	Hexamethylene diisocyanate	нмді	OCN — C <sub>8</sub> H 12— NCO
3	Isophorone diisocyanate	IPDI	H <sub>3</sub> C CH <sub>3</sub> CH <sub>2</sub> -NCO
4	4,4'-Methylene bis phenylene diisocyanates	MDI	OCN — Ph — CH 2 <sup>—</sup> Ph — NOC
5	Cyclohexane-1,4-diisocyanate	CHDI	
6	p-Phenylene -1,4 -diisocyanate	PPDI	

Table 1 - The most prevalent diisocyanates used in the manufacturing of polyurethane

(HDI), they discovered that the diisocyanate structure had a significant influence on the mechanical characteristics of the PUR.

They explained that the hard segment's symmetry and chemical makeup were to blame for the impact. Based on variations in the interatomic bond type, Caraculacu et al. [13] established a new general categorization of many probable isocyanate addition methods. Beginning with the most recent developments in physicochemical techniques, new information was discovered about the structure of isocyanates and the various hydroxyl compound relationships that resulted from additional procedures. It was discovered that the symmetrical

diols' intramolecular hydrogen bonding significantly influenced the two OH group reactivities.

### Polyols

Alcohols having several hydroxy groups are known as polyols, and they are the main reactants with isocyanates. These substances are characterized by their hydroxyl number (OH number, in mg KOH/g), which is inversely related to molecular weight. Based on their chemical makeup, polyols can be categorized as acrylic, polyester, polyether, or polycarbonate polyols. Polypropylene glycol (PPG), polyethylene oxide, or polyethylene glycol (PEG), and polytetrahydrofuran, or PTMEG, are the three categories into which polyether polyols fall. Polyols come in mixed aliphatic-aromatic and aromatic forms, as well as in both aromatic and aliphatic forms [14]. When compared to isocyanates, polyols typically have relatively low toxicity. The common polyol types are seen in Figure 4, with each type identified by its backbone structure. Nowadays, polyethers form the basis for over 75% of the polyols used to make polyurethane [15].

The final product's characteristics, polyurethane polymers, are greatly influenced by two essential properties of polyols: functionality and equivalent weight. The average number of functional groups that react to isocyanate in each polyol molecule is known as polyol functionality. The following definition of polyol equivalent weight is applicable:

Equivalent weight = Molecular weight of polyols/functionality of polyols = 56100/hydroxyl number

The hydroxyl number (mg KOH/g) is the number of milligrams of potassium hydroxide present in one

= 24 ===-

gram of polyols [16]. Acrylic polyols are typically employed in high-performance applications that need UV stability. Acrylic polyols are used in polyurethane coatings for automobile finishes because they are chemical resistant and long-lasting. The chemical composition of the monomers employed in acrylic polyol-based PU coatings has a significant impact. Figure 5 is an example of an acrylic polyol reaction preparation.

Polyols provide flexibility to the network chains' backbone, which is why they are referred to as soft segments or domains in PUs. Polyether polyols are the byproducts of a reaction between alkali initiators and monomers such as ethylene oxide and propylene oxide. Polyols utilized in polyurethane production are hydroxyl-terminated long-chain macroglycols with varying molecular weights [17]. The structure of polyol is an important aspect in determining polyurethane characteristics.

Polyols can be made from epoxy resins that have secondary hydroxyl groups [18]. Special silicone resins are ideal for heat-resistant PU coatings. Vinyl <u>polym</u>ers, alone or in conjunction with other polyols, can be utilized efficiently as polyols. Vegetable or plant oils, such as castor oil, linseed oil, tall oil, and others, can also be utilized as polyols. Because coal tar includes many groups containing active hydrogen, it may also be utilized to make polyols.

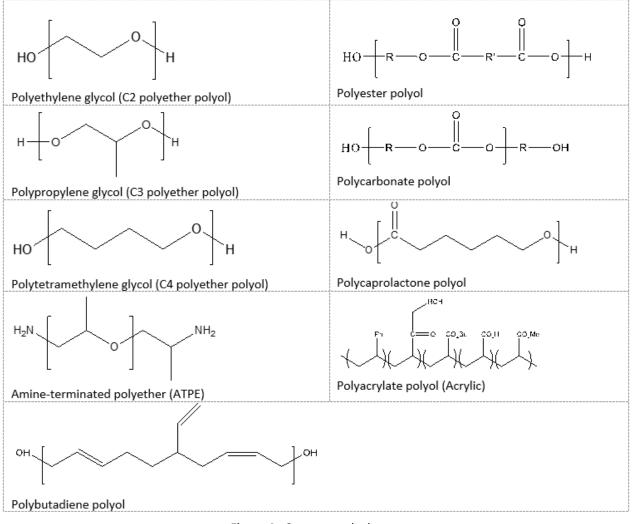


Figure 4 - Common polyol types

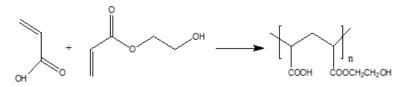


Figure 5 - Preparation of acrylic polyol

\_\_\_\_\_ 25 \_\_\_\_\_

Polyester polyols can be made using a variety of methods, including polycondensation of hydroxyl acids or diacids and diol or ring-opening polymerization of lactone. Polyester produced from a combination of two or more diacids reacting with various glycols is a popular commercial product [[19], [20]].

The invention describes polyester polyols with an average equivalent weight between 200 and 4,000. These polyols are made by reacting alpha and omega dicarboxylic acids with butane 1,4-diol, hexane 1,6-diol, propane 1,3-diol, or pentane 1,5diol. The resulting polyols with three to six hydroxyl groups are then used to create PUR pourable elastomers with enhanced resistance to hydrolysis [21].

The molecular weight and structure of soft segments also affect polyurethane shape. Typically, soft segments with average molecular weights of 1000–5000 are used in the manufacturing of thermoplastic polyurethanes. Phase separation is greater in polyether urethanes than in polyester urethanes due to the reduced compatibility of the polyether soft segments with the polar hard segments.

Both polyester urethane and polyether exhibit changes in characteristics as soft segments' molecular weight is increased. The impact of increasing the molecular weight of the soft segment on the microphase separation and viscoelastic characteristics of polyester polyurethanes was investigated by Velankar and Cooper [22]. DSC, SAXS, and rheology were used to describe a range of polyester urethanes with variable block lengths (soft segment MW = 830, 1250, 2000, and 3000) and constant composition (soft segment  $\approx$  50 wt%). PUs made with SS MW 830 and 1250 were single-phase materials, according to DSC and SAXS data.

These two PUs exhibited rheological behavior that was similar to homopolymer melts and reasonably consistent with Rouse's theoretical predictions. The amount of microphase separation increased gradually with SS MW, according to DSC, SAXS, and rheological study (Time Temperature Superposition) for PUs with SS MW 2000 and 3000. Furthermore, a substantial relationship between soft segment length was observed for both the relaxation time and the Newtonian viscosity.

Korley et al. [23] investigated the effects of crystallinity in the soft segment phase, which is made up of polyether soft blocks with varying inclinations toward crystallization. The authors of this work looked at the morphology and mechanical behavior of a range of polyurethanes with different hard segment contents that contained PEO (1000 and 4600 g/mol) and PEO-PPO-PEO (1900 g/mol) soft segments. In comparison to polyurethanes including PEO-PPO-PEO soft segments, it was shown that toughness was enhanced and the storage modulus of polyurethane below the Tm of the soft block was raised by soft segment crystallinity in PEO (1000 g/mol). The results of the study demonstrated that organized soft segment areas, which dissipate energy and contribute to the overall deformation process, not only provide extensibility but also reinforce the polyurethane matrix during the process.

Strictly speaking, the urethane process is catalyzed if the catalysts raise the rate of reaction without getting consumed themselves. The most often utilized catalysts are tertiary amines, such as tetramethyl butane diamine (TMBDA) and 1,4-diazo bicyclo (2,2,2)-octane (DABCO), and organo compoundsound, such as dibutyl tindilaurate (DBTDL).

A segmented structure with flexible, polyol chains, and rigid segments, as well as segmental length, crystallizability, intra- and inter-segment hydrogen bonding, interactions like overall compositions, and molecular weight, are the characteristics of polyurethane resins [24]. Polyurethane has unique mechanical, thermal, and elastomeric qualities because of its hydrogenbonding architecture. Because of its flexible chain and lower glass transition temperature than room temperature, the polyester section is referred to as the "soft segment." Instead of a covalent bond being chemically cross-linked, polyurethanes include a large number of hydro gross linkages, which allow them to rearrange upon mechanical deformation [25]. After the tension is released, the hydrogen bond reorganizes and regains its deformation strength. Urethane coatings have a limited capacity for self-healing due to intermolecular hydrogen bonding. This characteristic makes it possible to create polyurethanes that are resistant to solvent swelling and abrasion. Foams, coatings, adhesives, and thermoplastic elastomers are just a few of the applications for polyurethane, a special polymeric substance with a broad variety of physical and chemical characteristics (1–10). Polyurethane holds prominent place in various applications, а particularly in the coating sector, due to its highquality coating layer that exhibits resistance to weather stability, and mechanical solvents, qualities. The polyurethane coatings industry comprises two main systems. One is referred to as a one-component (1K) system, where the substrate is

= 26 =

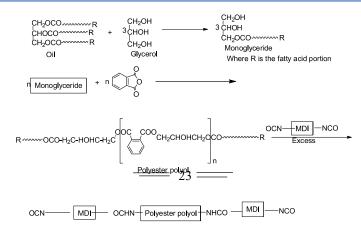


Figure 6 - Reaction sequence of the preparation of polyurethanes



Figure 7 - Green PU coating from Niger-seed oil

physically cured after being covered with high molecular weight polyurethane. The other system consists of two components, hydroxyl functional polymers, and polyisocyanate hardeners with an ng NCO group.

To create monoglycerides, polyester polyol was made using esterified soybean oil and a glycerol:1:3 molar ratio [26]. Polyester polyols were created using a ratio-based reaction between the produced monoglycerides and phthalic anhydride. To create polyester–polyurethane coatings, PU prepolymer (Figure 6) was created by polyaddition reaction of diphenylmethane diisocyanate with polyester polyols at NCO/OH ratios of 1.2, 1.4, and 1.6 using toluene as a solvent. A high NCO/OH ratio is generally considered typical since it results in tougher, more solvent-resistant coatings. The produced coatings exhibited attributes such as chemical resistance, impact resistance, pencil hardness, and flexibility. As the number of hard segments in the sample increases, so do the produced coatings' favorable attributes.

Velayutham et al. [[27], [28]] used polyester polyols with varied oleic acid concentrations to create PU coatings. To create PU coatings, the polyols reacted with aromatic isocyanate (toluene 2,4-diisocyanate, or TDI). The physical characteristics of PU coatings on mild steel panels were examined about different NCO/OH ratios and polyols' oleic acid concentrations. Physical-chemical characteristics such as solvent resistance, adhesive qualities, drying time, pencil hardness,

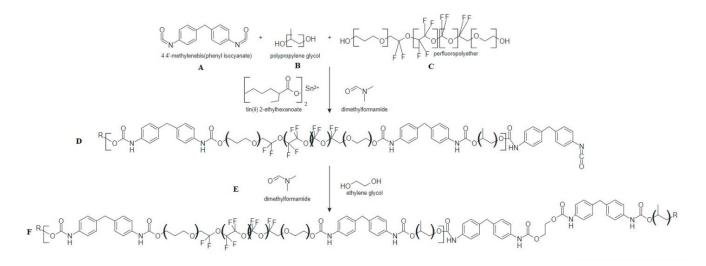
corrosion/chemical resistance determination, and solvent resistance were described together with the characterization of PU coatings using IR spectroscopy analysis. The best overall coating qualities are shown by the coatings made from polyol with a 28% content. The mechanical and anticorrosive capabilities of all the coatings increased progressively as the NCO/OH ratio rose.

Niger seed oil (NSO) was used by Ranjeet et al. [29] to create a PU covering (Figure 7). Niger seed oil is amidated with diethanolamine to create polyesteramide polyols, which are then esterified with several biobased dicarboxylic acids (phthalic, itaconic, and dimer) to add the necessary hydroxyl group functionality. Hexamethylene diisocyanate biuret (HDI-B) and synthetic polyesteramide polyols are used to make the polyurethane coatings. The gel content method is used to show the cross-link density of PU coatings, and the saltwater immersion technique is used to conduct the corrosion investigation. By using differential scanning calorimetry and thermogravimetric analysis, the glass transition temperature (Tg) and thermal stability of the PU coatings are also investigated.

Common polymeric coatings like polyurethane offer surfaces in the food processing, marine, and biomedical sectors flexibility, durability, and resistance to abrasion (Figure 8). Because of its adjustable chemistry, polyurethane has enormous potential for materials of the future. Many studies have been conducted on the modification of polyurethane to provide it additional properties like antibacterial, non-fouling, anticorrosive activity, or high heat resistance. Traditional solvent-borne polyurethane (PU) based on 4,4'-Methylenebis (phenyl isocyanate) (MDI), which is often used in food processing facilities, boat hulls, and floor coverings, was produced by Rudlong and Goddard 2023 [30]. The polyurethane included 1%, 2%, and 3% perfluoropolyether (PFPE).

Wetability and hydrophobicity were assessed using a dynamic water contact angle. The addition of perfluoropolyether blocks (PU–co–1PFPE 131.5° ± 8.0, PU–co–2PFPE 130.9° ± 5.8, and PU–co–3PFPE 128.8° ± 5.2) significantly advanced the water contact angle in comparison to the control polyurethane (93.6° ± 3.6). The surface orientation of fluorine provided support for the lower critical surface tensions of PU–co–3PFPE-modified polyurethane (12.54 mN m-1 as opposed to 17.19 mN m-1 for unmodified polyurethane).

Because of its superior mechanical and thermal qualities as well as outstanding chemical resistance, epoxy resins find extensive usage in the adhesive, automotive, paint, and aerospace sectors. Nevertheless, the overall impact resistance of these materials is weakened following external impact due to the propagation of cracks in epoxy polymers. As a result, many impact modifiers have been created to lessen epoxy polymers' brittleness. Polyurethanes (PU) can increase the toughness of polymers by acting as impact modifiers. While the fact that polyurethanes (PUs) phase-separate in the polymer matrix during curing is widely known, it has proven difficult to reattach PUs to the matrix to improve the mechanical characteristics of polymers.



**Figure 8** - A two-step prepolymer reaction of MDI (A), PPG (B), and PFPE (C) forms the prepolymer (D). Chain extender (E) added to form final PU–*co*–PFPE polymer (F).

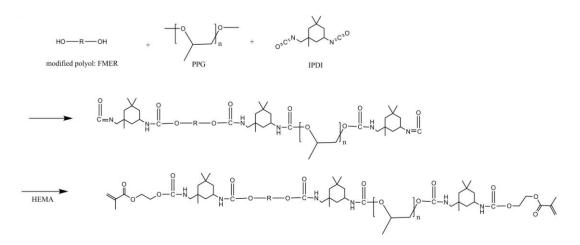


Figure 9 - PU reaction strategy including the reaction of isophorone diisocyanate (FMEP-PU) with hydrogenated epoxy polyol modified by fatty acids

Unlike previous research that concentrated on changing capping agents to establish a network topology between the polymer matrix and PU, Kim et al., 2019 [31] included epoxy functional groups into polyol backbones. By using gel permeation chromatography, we were able to verify the molecular weight of the produced PU. Additionally, the produced material was mixed with the epoxies, and the resultant materials' mechanical and thermal characteristics were assessed. We also measured impact resistance, flexural strength, and tensile strength. The impact strength and mechanical strength of the epoxy compositions were improved and sustained up to 10 phr of PU by the addition of PU (Figure 9).

In 2019, Zaimahwati et al. [32] polyurethane (PU) nanocomposite that has been prepared using castor oil and coated with montmorillonite nanoparticles. After synthesizing polyols from castor oil and organic montmorillonite nanoparticles, polyurethanes (PU) were prepared, evaluated, and used as coating materials for polyurethane nanocomposites. Organic montmorillonite nanoparticles were added to polyols to create a polyurethane nanocomposite, which was then combined with toluene diisocyanate. Using thermogravimetric analysis (TGA) equipment, the thermal properties of polyurethane nanocomposites were used to evaluate their efficacy as heatresistant coatings. Subsequently, the adhesive strength and morphological characteristics of the material coating were assessed. The results showed that the addition of montmorillonite improved both the adhesive strength of the material coating applied to the material's surface and the heat resistance of the material's film surface layer.

The impact of diisocyanate symmetry and hydrogen bonding on microphase morphology was examined by Yilgor et al. [33]. Their investigation into segmented polyether ureas and non-chain extended polyether urethanes produced some intriguing findings on the microphase separation of these polymers. The researchers observed that polyurethanes prepared with symmetrical diisocyanates, namely 1,4-phenylene diisocyanate (PPDI), 1,6-hexamethylene diisocyanate (HDI), and 1,4-cyclohexyl diisocyanate (CHDI), exhibited a microphase morphology in which the soft segment matrix was permeated by hard segments that resembled ribbons. Conversely, polyurethanes based on diisocyanates that are not symmetrical, such as 1,3-phenylene diisocyanate (MPDI), 2,6- and 2,4-toluene diisocyanate (TDI), bis (4-isocyanate cyclohexyl)methane (HMDI), and MDI, did not exhibit microphase morphology at ambient temperature. All polyether areas, in contrast to their urethane counterparts, showed microphase morphology at room temperature, irrespective of the diisocyanate's structure or symmetry. Their research demonstrates the critical influence that hard segment symmetry has on polyurethane microphase formation. PU coatings are available in several varieties. Solvent-based coatings, or conventional PU coatings, have dominated the industrial coating industry in recent decades. More restrictive laws about volatile organic compound (VOC) emissions, however, nevertheless pose a threat to this position. Because of this, producers of paint and suppliers of raw materials are creating substitute technologies that work just as well but are more environmentally friendly.

Coatings containing volatile organic compounds (VOCs) are becoming more and more appealing since they offer excellent protection and address environmental issues. Eco-friendly polyurethane coatings include a subclass known as polyurethaneurea hybrid coatings [34]. The reason for the interest in this kind of coating is that it has been claimed to have better mechanical qualities than traditional polyurethanes, which improves the organic film's overall performance [35]. An important part of this scenario involves high-solid systems. Hybrid coatings made entirely of solid polyurethane and urea have been created in this work. Different NCO/OH molar ratios and methylene diphenyl diisocyanate (MDI) were used in the preparation of the coatings. By employing differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS), the impacts of the structural properties on the physical aging behavior and the electrochemical responsiveness of the hybrid coatings were assessed. The optimum combination of attributes, including low sensitivity to physical aging and excellent corrosion resistance, was demonstrated by the coating with the greatest NCO/OH ratio, according to the findings [36]. The kind of diisocyanate and the NCO/OH molar ratio affect the performance of polyurethane and polyurethaneurea hybrid coatings [[37], [38]]. Mishra and colleagues (2019) noted that increased NCO/OH ratios also resulted in enhanced heat stability for PUbased coatings. According to Negim et al. [39], elongation at break and viscosity declined as the NCO/OH ratio rose, while the tensile strength, hardness, and rip strength of water dispersion polyurethanes escalated. In addition to the urethane/urea hard components, this behavior is linked to the increased production of molecular groups such as allophanate or biurate connections [40].

Two-step solution polymerization was used to create а variety of moisture-cured polyurethane/polysiloxane (PUs) copolymers (Figure 10). Alkoxysilane was utilized as an end-capping agent, and amine-terminated polysiloxane (PDMS) and polyester diol were combined as mixed soft segments to react with a 4,4'-diphenylmethane diisocyanate (MDI). The impact of changing building block structures, such as the NCO/OH ratio and polyester diol structure, on the characteristics and morphology of polyurethanes (PUs) were investigated. Investigations were conducted into the tensile, dielectric, thermal stability, surface, and water-repellent qualities. The findings demonstrated that differences in molecular architecture had a significant impact on the appearance and characteristics of PUs [41].

Without the use of a catalyst or solvent, Prabhakar et al., 2005 [42] synthesized NCOterminated polyurethane of polypropylene glycol (PPG)-1000 and isophoron diisocyanate (IPDI) with an NCO/OH ratio of 1.2:1. The produced prepolymer was structurally investigated using 1D and 2D NMR spectroscopy. To provide a clear description of the assessment of the urethane groups and to

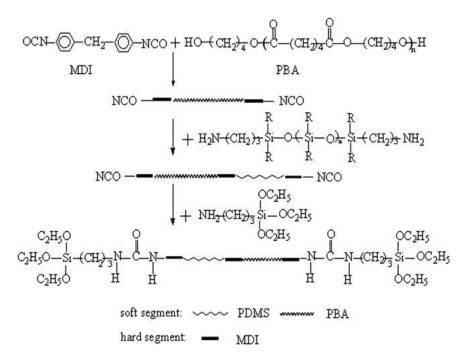


Figure 10 - Synthesis of the polyurethane/polysiloxane copolymer

== 30 ===-

track the reactivity of isocyanate groups with the hydroxyl function of PPG, 1H NMR spectra, and dibutyl amine back-titration were employed. 13C NMR spectroscopy was used to crosscheck the % conversion data for the methanol end-capped prepolymer in the urethane zone. The secondary NCO group is more reactive than the primary group, according to the findings.

In 2003, [43] Semsarzadeh and Navarchian synthesized Poly(urethane-isocyanurate)s created by reacting poly(propylene glycol) and toluene diisocyanate at varied stoichiometric ratios (1-3) with varying amounts of ferric acetylacetonate (FeAA) and dibutyltin dilaurate (DBTDL). Using Fourier transform IR spectroscopy, the impact of the catalyst type and concentration, as well as the NCO/OH ratio, on the degree of urethane and isocyanurate synthesis were investigated. With a rise in the stochiometric ratio or DBTDL concentration, it was seen that the proportion of the trimer group and the trimer/urethane content rose. Thermogravimetric (TG) analysis was used to examine the thermal breakdown of the polyurethanes in an inert environment.

The TG curves showed three phases of disintegration, with 355 to 385 °C serving as the major degradation temperature. The effects of the NCO/OH ratio, catalyst type and concentration, and heating rate on the thermal stability of the polyurethanes were determined. We estimated the activation energies of thermal decomposition by use of the Kissinger, Flynn-Wall, and Ozawa methods. The swelling behavior of solid polyurethanes in toluene showed that as DBTDL concentration and/or NCO/OH ratio increased, the crosslink density increased and the swelling ratio and average molecular weight between crosslinks decreased. It was demonstrated that the sol fraction of solid polyurethanes decreased with an increase in the stochiometric ratio or the amount of DBTDL.

Rummi et al. (2013) [44] studied that by reacting a molar excess of diphenylmethane diisocyanate (MDI) with polypropylene glycol (PPG) for two hours at 60°C, polyurethane prepolymers were produced. It investigated how different NCO/OH molar ratios and polyol molecular weights affected the polyurethane plaster cast's tack-free time, setting time, diametral compression strength, percent elongation, and tensile strength. When the NCO/OH molar ratio increases, the cast's tack-free period and setting time reduce but its diametral compression strength increases. Using a universal testing apparatus, tensile strength was determined to increase as the NCO/OH ratio increased, even though the percentage of elongation had the opposite tendency. As the polyol molecular weight rises, the cast's tack-free and setting times increase while its diametral compression strength decreases. The tensile and diametral compression strengths of blended polyols, such as PPG 1000 and PPG 400 mixed in a 50/50 ratio, are equivalent to those of their unblended equivalents. Compared to fiberglass cast, polyester cast has a higher % elongation and diametral compression strength.

Polyaniline/graphene was used as an anticorrosion filler by Kewen et al., 2016 [45] to create a conductive coating based on aqueous polyurethane. Potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS), and salt spray were used to evaluate the coating. The maximum conductivity for polyurethane coating was achieved with a polyaniline/graphene ratio of 0.75 wt% and a graphene concentration of 4 wt%. Youtong Wu et al., 2019 [46] used SG-ZP mixtures as an additive to create an aqua polyurethane-based surface. Tafel curves and EIS analysis were used to test the obtained coating. The 0.5 wt% sulfonated graphene/zinc phosphate ratio produced satisfactory results, with a corrosion current density of 0.4252  $\mu$ A/cm2 and a charged transfer resistance (Rct) of 10.937 103 cm2. Cui et al., 2020 [47] investigated if smart anticorrosion coatings outperformed traditional ones. The paper introduced the linked ideas of self-healing and nanocontainer development. The present issues, their optimization, and potential future consequences have all been explored.

Pei-Ying Tsai et al., 2018 [48] used a complex PU/Gr coating with a ratio of 0,2,4, and 8wt.% for Gr. The anti-corrosion and mechanical capabilities of the mixture were evaluated using EIS, salt spray, and cross-cut tests. At normal conditions, anti-friction properties were evaluated using a tribometer and the ball-on-disc technique. Complexes containing 4 and 8% gr. The friction coefficient data showed that increasing the graphite (Gr) content to 8% reduced the anti-friction qualities of the PU/Gr composite coatings by 61% compared to the standard coating.

Thi Xuan Hang et al., 2015 [49] showed that treatment with 2-aminoethyl-3aminopropyltrimethoxysilane (APS) resulted in the precipitation of nanosized ZnO. ZnO-APS nanomaterial characterization was performed by UV-Vis, SEM, TEM, and XRD spectroscopy. Under

== 31 ====

QUV testing conditions, the degradation of polyurethane coatings containing nano ZnO at a weight percentage of 0.1 and nano ZnO-APS at two weight percentages, 0.1 and 0.5 wt%, was assessed. The findings demonstrate that the nano ZnO-APS particle sizes range from 10 to 15 nm and have a spherical shape. The polyurethane coating's UV resistance was enhanced by nano ZnO, and its effectiveness was further enhanced by surface modification using APS. Notably, the UV resistance of the polyurethane coating was markedly enhanced by the addition of nano ZnO-APS at 0.1 wt%.

Huibin Zhu et al., 2020, [50] used a one-step spray-coating approach to develop superhydrophobic films with flexibility, mechanical robustness, and thermal stability. The coatings, which had a micro-nano structure and a Tg greater than 221°C, kept contact angles over 150 degrees. They were extremely flexible, with a friction value of 1.70. Electrochemical corrosion studies indicated their extraordinary resistance (Icorr reaching 8.90 x 10-5 A cm-2 under particular conditions), making them promising for harsh environment applications.

Yao Tong et al. 2017, [51] investigated the use of graphite and graphene particles to improve the specific conductance anti-corrosion and characteristics of polyurethane (PU) coatings. In terms of electrical conductance, a hybrid composite including carbon nanotubes outperformed single filler systems, with a significant advantage reported at 5 wt% loading (0.77 S/m, whereas the single filler system remained non-conductive). The conductive mechanism has been discovered. Lower filler loadings in the coatings increased anti-corrosion properties. Resistance readings from Electrochemical Impedance Spectroscopy (EIS) and the four-point probe technique were compared and discussed.

Mahmudzadeh et al. 2019, [52] investigated a cost-effective and ecologically friendly approach for decreasing graphene oxide in an hour using Urtica dioica leaves extract at 90°C. The elimination of oxygen functional groups was verified by Raman spectroscopy. Even after accelerated weathering, the decreased graphene oxide increased the corrosion resistance of polyurethane coatings and displayed remarkable protection efficacy, topping 99% in low-frequency impedance studies.

Xiaoyun Yea et al., (2019), [53] demonstrated the fabrication of zinc oxide (ZnO) array/polyurethane (PU) nanocomposite coatings on stainless steel substrates. ZnO arrays were grown from seeds and then mixed with PU. The coatings' structure, wettability, mechanical characteristics, and corrosion resistance were all evaluated. The ZnO arrays have a hexagonal wurtzite structure and are somewhat more hydrophilic. Mechanical qualities improved as ZnO concentration increased, and the coatings demonstrated good corrosion resistance.

coatings demonstrated good corrosion resistance. Infrared radiation performance improved slightly as well. This innovative organic/inorganic nanocomposite coating is a viable strategy for creating functional coatings with improved corrosion resistance and mechanical properties in a variety of polymer systems.

Hui Wang et al., (2021) [54] investigated a novel anticorrosive coating capable of self-healing in the event of damage. Using Diels-Alder (DA) bonding, a PU prepolymer is combined with a modified CeO2 furan to form this covering. These DA bonds are efficient in preserving mild steel against corrosion following coating degradation. The photothermal characteristics of dopamine allow this coating to self-heal in settings similar to infrared irradiation for 20 seconds. The mechanical and anticorrosive properties of the coating remained nearly unaltered after such self-healing. The proposed coating (PU DA-d@CeNPs5) exhibited good mechanical properties (38.89 ± 0.52 MPa), adhesion qualities (12 MPa), and an impedance modulus at 0.01 Hz equivalent to  $1.29 \times 109$ -ohm cm<sup>2</sup>. Even after 100 days of continuous immersion, the impedance modulus at 0.01 Hz can still surpass 107 ohms/cm2.

Polyurethane foam waste (PUR) was used and treated with dicarboxylic acids (DA) by Godinho et al., (2021) [55]. Using spectrum analysis, the ratio of PUT and DA was regulated, and the findings indicated that the recycled polyol (RP) has an appropriate hydroxyl number and acidity to form a new polyurethane (PU). This novel substance was utilized to make polyurethane coatings for wood (PUC). When compared to a typical polyol coating, the coating generated from RP has a higher hardness, but less gloss and more hydrophobicity.

Hui Yuan et al. [56] investigated the influence of water-based polyurethane, silicon dioxide, and fillers on the characteristics of modified silicate coatings. Coatings containing 10% polyurethane and 4% silica demonstrated superior mechanical qualities as well as resistance to heat and acids. The changed coatings outperformed the unmodified coatings in terms of strength, heat resistance, and acid resistance by 25.1%, 34.1%, and 32.4%, respectively. A thick microstructure with an interpenetrating network was revealed by microstructural investigation. The coatings were also found to be less permeable, which increased their properties. Heat resistance at high temperatures (250°C) was fulfilled by the modified coatings.

Fengyuan Zhanga et al., (2020) [57] effectively created water-based polyurethane composites (WPC) containing functionalized graphene oxide (PAFG) generated from polyethyramines. The inclusion of nanoparticles at the optimum concentration improved the characteristics of WPU composites significantly. In comparison to pure WPU, the contact angle with water and water absorption in the WPU composite improved significantly to 98.5°C and 3.01 wt.%, respectively, from 70.5°C and 8.31 wt.%. Furthermore, there were significant improvements in thermal stability and mechanical qualities, particularly with the addition of 0.05 wt.% PAFG. With a 10% mass loss, the decomposition temperature of the WPU composite climbed to 322°C, which was 29.3°C higher than that of pure WPU. When compared to pure WPU, the tensile strength of WPU containing 0.05 wt.% PAFG improved by 130.92%. In terms of electrochemical data, after 31 days of immersion, the |Z| value at 0.01 Hz for WPU dropped, whereas WPU/PAFG0.05 remained steady. This demonstrates that 0.05 wt.% PAFG significantly improves the barrier characteristics of the WPU coating.

Jiahua et al., (2012) [58] used the sol-gel process to construct fluorescent silica shells of varying thicknesses on spherical carbonyl iron (CIP) particles. For metal particle surface compatibility with TEOS, hydrolysis, and condensation of tetraethyl orthosilicate (TEOS) were combined with the gelatin В and usage of 3 aminopropyltriethoxysilane (APTES). This results in a protective silica shell with variable thickness. The silica shell increases the particles' anti-corrosion and heat resistance. SIP and CIP-silica self-healing polyurethane coatings demonstrated increased anticorrosion and heat resistance.

Tuan et al., (2022) [59] researched a novel anticorrosive coating that may self-repair when damaged. This coating is made of polyurethane acrylate (PUA) with lithium salt added as a polymer electrolyte. UV radiation was used to approve PUA and lithium salt mixtures, resulting in thin coatings with high heat resistance and ionic conductivity. The best conductivity was exhibited by PUA with a 25% mass fraction of lithium salt. The coating's mechanical and structural properties, as well as its capacity to self-heal under near-infrared illumination, were also investigated.

Cheng et al., (2020) [60] created and tested ecologically friendly non-isocyanate polyurethane (NIPU) anti-corrosion coatings. The synthesis and formulation of these coatings employing several materials, including amine terminated NIPU, TEOS, and BPA epoxy, are the main emphasis of this work. The study evaluates the anti-corrosion performance of NIPU coatings with varying TEOS concentrations and finds that the best anti-corrosion behavior was shown by coatings containing 5% TEOS. Spectroscopic and microscopy methods have demonstrated that variations in anti-corrosion performance are related to the organic/inorganic micro-phase separation.

This research advances our understanding of how TEOS affects the anti-corrosion properties of NIPU coatings. Pavan et al., 2021, [61] investigate the synthesis of bio-renewable materials such as vegetable oils, outlining chemical changes and prospective uses. The analysis also tackles the obstacles and promising technology in the ecofriendly transition of the coatings sector.

Aqdas et al. (2015) [62] emphasize the benefits of ecologically friendly waterborne polyurethane (WPU) coatings, such as reduced VOC emissions and desired characteristics. It goes over current advances in WPU coatings, such as UV-cured and hyper-branched polyurethanes. It also investigates strategies to improve mechanical strength and flame retardancy using additives such as nanoparticles and fire retardants. By incorporating two commercially available inhibitors, Ravindra et al., 2015, [63] increased the anti-corrosive capabilities of polyurethane coatings. The encapsulating technique and its impacts on coating performance are explored, and improved corrosion inhibition efficiency is demonstrated.

Jing Li et al. (2016), [63] discovered that adding the following chemicals to a waterborne polyurethane matrix in the following order improves the anticorrosive characteristics of polyurethane: graphene oxide, moderately reduced graphene oxide, and functionalized graphene. Impedance Electrochemical Spectroscopy and salt spray testing confirmed that the additives are anti-corrosive. The chemical and dispersion states of graphene within polyurethane, according to the findings, impact the material's capacity to resist corrosion. The inclusion of 0.2 wt% of reduced graphene oxide improves the

\_\_\_\_\_ 33 \_\_\_\_\_

anticorrosive capabilities of graphene-reinforced SEM a polyurethane composite coatings. The findings of the Electrochemical Impedance Spectroscopy demonstrated that, after 235 hours of immersion in a 3.5 wt% NaCl solution, there was no under-

painting corrosion and that the impedance modulus at 0.1 Hz was constant at 109 U. This was true over the whole 235-hour period, with very little variation noted.

When 0.2 wt% reduced graphene oxide is added, the anticorrosive properties of graphene-reinforced polyurethane composite coatings are enhanced. After 235 hours of immersion in a 3.5 weight percent NaCl solution, the findings of the Electrochemical Impedance Spectroscopy revealed that underpainting corrosion did not occur and that the impedance modulus at 0.1 Hz was constant at 109 U. This was true throughout the whole 235-hour period, with very little variation detected.

According to Ashraf et al. (2015) [64], a Transmission electron microscopy image indicated that zinc oxide nanoparticles generated by direct precipitation have a pseudospherical shape and diameter of roughly 20.0 nm. Zinc oxide nanoparticles are uniformly disseminated in polyurethane by ultrasonication at loading levels ranging from 0.1 to 2.0 wt.% to improve polymer characteristics. The coatings were shown to be efficient at inhibiting both Gram-positive and Gramnegative bacteria growth. When ZnO NPs are used, the number of organisms growing on the coating's surface decreases. Moreover, better mechanical and corrosion resistance at lower concentrations was obtained by increasing the weight % of ZnO NPs. Scanning electron microscopy data served as the foundation for the conclusions.

Pooneh et al. (2018) [65] showed that the covalent functionalization of graphene oxide nanosheets 3-glycidyloxypropyl) by trimethoxysilane additions contributes to the improvement of mechanical performance and corrosion resistance. The study of nanomaterials was conducted using Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD). The physicalmechanical characteristics of the coating with nanosheets were assessed by the use of tensile tests and dynamic mechanical thermal analysis (DMTA). In addition, the impact of GO and fGO nanosheets on the surface fracture morphology of polyurethane coating during tensile testing was investigated using SEM analysis. The results of the study showed that the addition of fGO nanosheets enhanced the mechanical, anti-corrosion, and physical properties of the PU coatings by fortifying the interfacial bonds between the coating and the GO nanosheets. To understand the mechanism of the trimethoxysilanepolyurethane interaction, GO surface quantum mechanics techniques were used.

According to research by Abhijit et al., 2020 [66], polyurethane is a very versatile material that can be created to order when additives and nanoparticles are added. This enables a wide range of properties, including soft-touch coatings and rigid construction materials. The material's mechanical, chemical, and biological characteristics may be adjusted to meet specific needs, which has piqued the interest of several businesses as well as the scientific community. The chemistry of the constituent parts of polyurethane is examined in this study, along with recent advancements and applications in the medical, automotive, coatings, adhesives, sealants, paints, textiles, marine, wood composites, and apparel sectors.

Xiaohua et al., 2013 [67] demonstrated that LiproITM, a bio-based polyol, was made using a variety of vegetable oils. The oligomer dispersion and chemical structures of these polyols were investigated. The polyols were used to create polyurethane coatings with a bio-based content of about 60%. The coatings exhibited satisfactory mechanical and thermo-mechanical properties. The flax PU, which comes from oil that has a high linolenic acid content, had the highest performance because of its low solvent swelling, high glass transition temperature, strong cross-linked networks, resistance to abrasion and water, and hardness.

The goal of this investigation was to determine how various hardeners influenced the protective properties of polyurethane coatings, as investigated by Ewa et al. 2014 [68]. It was necessary to comprehend any modifications to the mechanical qualities, crosslink density, and chemical structure. After being applied to mild steel panels, the wet adhesion, abrasion resistance, and anti-corrosive properties of unpigmented polyurethane coatings with different hardener concentrations were evaluated. The electrical and abrasion resistance of coatings with a greater hardener ratio was demonstrated by the findings. The coating with the stoichiometric hardener ratio exhibited the least degree of adherence. According to the FTIR data, the coatings' urethane group count dropped when the hardener ratio dropped. The study concluded that electrochemical impedance spectroscopy and DC resistance are helpful methods for determining how well the coatings will hold up over time.

The combination of poly (ethylene glycol) with epoxidized vegetable oil has been researched by Mandar et al., 2015 [69] to create novel polyester polyols. A sustainable method of extracting oil from cottonseed and karanja was used. The molecular weight of the poly (ethylene glycol) was altered. The polyols' spectrum properties and end groups were looked at. These polyols were utilized to replace dipen tene with xylene in ecologically friendly polyurethane coatings. Along with their physical and thermal characteristics, the resultant polyurethanes were evaluated for adhesion, gloss, hardness, impact resistance, and flexibility. These coatings showed promise for industrial use.

Tsao-Cheng Huang and colleagues (2017) [70] investigated the feasibility of ZrP/PU nanocomposite films to ensure consumption security. The electrochemical experiments confirmed the improved consumption resistance of ZrP/PU coatings on steel surfaces as compared with pure PU coatings. The connecting of ZrP nanoplatelets into the PU lattice further strengthened dampness obstructing characteristics. Ying Liang et al. (2020) [71] investigated the use of polydimethylsiloxane and acetylated starch in the manufacturing of biobased polyurethane coating. The research was done and it was found that an acetylated starch-based polyurethane coating with а 0.5-3% polydimethylsiloxane content has anti-corrosion properties.

enhancement of the The anti-erosion characteristics of aluminum (Al) coatings by the creation of superhydrophobic surfaces was examined by Xiuyong Chen et al. (2014) [72]. The cycle involves using a suspension fire splashing technology to save polyurethane (PU)/nano-Al2O3 composites by first curve showering Al coatings onto steel substrates. The result is the successful production of superhydrophobic PU/nano-Al2O3-Al coatings with a large spectrum of consumption that are safe. The super hydrophilicity/superhydrophobicity of the coatings may be adjusted by varying the concentration of PU in the initial suspension. A specific layer with 2.0 weight percent PU exhibits excellent hydrophobicity, with water droplets sliding at around 6.5°C and making contact at about 151°C.

For maritime foundations, the PU/nano-Al2O3-Al coatings with their solid enemy of consumption capabilities and superhydrophobic qualities can be employed as protective layers.

Four polyurethane saps—polyurethane (PU), epoxy-changed polyurethane (EPU), fluorinated polyurethane (FPU), and epoxy-altered fluorinated polyurethane (EFPU)-were used to create natural cement for the production of coatings with low infrared emissivity, according to a review by Yajun Wang et al. (2011) [73]. It is anticipated that the investigation will examine how these various tar networks affect the guarantee of low infrared emissivity coatings' usage. A neutral salt shower test has been employed to assess the goal, and coatings have been examined using Fourier-change infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Remarkably, the natural glue EFPU covering consolidating demonstrated exceptional erosion resistance. The simultaneous existence of epoxy aggregates and nuclear fluorine in the EFPU fastener was attributed to this improved presentation.

Fluorine-containing epoxy (FO) compounds that were combined using 2,2,3,3-tetrafluoro-1-propanol (TFP) and epichlorohydrin (ECH) in a single step were investigated by Xia Wang et al. (2015) [74]. A controlled sub-atomic weight fluorinated polyglycol produced by cationic polymerization. was Fluorinated polyurethane (FPO) and FO designs were detailed using techniques such as gel pervasion chromatography (GPC), FTIR, and NMR. Then, using a room temperature relieving procedure, FPO and diphenylenediisocyanate (MDI) were methyl combined to make a two-part fluorinated polyurethane coating. The concentration also evaluated the film surface using SEM (filtering electron microscope) imaging, as well as protection against the salt spray and water resistance.

The combination and representation of siliconebased covering materials that combine siloxane and polyurethane/polyurea copolymer were studied by Anna M. Mikhailova et al. (2012), [75]. Primary study, subatomic representation, warm properties, mechanical qualities, attachment, morphology, and consumption execution are all covered in the analysis, which reveals that aspects other than those covered in the hard part have an influence on the defensive and anticorrosion characteristics. To evaluate these covering materials' defensive and anticorrosion qualities, electrochemical impedance spectroscopy (EIS) was used. Indeed, the assessment

demonstrates that the hard part content does not apply only to these qualities. FT-IR spectroscopy was used to study the formation of the pre-blended copolymer and the ensuing siliconepolyurethane/polyurea copolymer (SPPU) with varying hard fragment (HS) percentages.

In their study on the enhancement of polyurethane-urea coatings, Yixing Zeng et al. (2023), [76] emphasized the importance of the isocyanate file in fitting the properties of polyurethane-urea coatings, providing a methodical approach to safeguarding metal and metal offices while encouraging the practical application of harmful to destructive materials. The coatings were assembled using conductive mica particles as fillers and aromatic isocyanate, amino-ended polyether, polyol derived from castor oil, and polyaspartic pitch as reactants. The review investigated how the isocyanate file affected the polyurethane-urea coatings' synthetic structure, static conductivity, and consumption hindrance. Higher cross-connectivity inside the covering was achieved by expanding the isocyanate file, albeit at the expense of decreased smallness and electrostatic conductivity. The organization of carbon dioxide increases in the overlying layer was blamed for this alteration. Salt shower tests and electrochemical impedance spectroscopy revealed that when the isocyanate record increased, the covering's ability to counterconsume on entire surfaces increased, but its appearance in areas with abandons decreased. Coatings with an isocyanate list of 1.0-1.1 demonstrated excellent electrostatic conductivity and erosion resistance, making them suitable for protecting metal and metallic workplaces.

To improve the enemy of consumption properties due to hydrophobicity and obstruction impacts, Mengting Moa et al. (2016) [77] developed functionalized graphene-supported polyurethane coatings with explicit surface surfaces. This resulted in less water contact and further developed the dispersion opposition of harmful substances. To improve their adversary of consumption qualities, the review focuses on the creation of PU nanocomposite coatings supported by functionalized graphene (FG). Its anti-erosive characteristics were further enhanced by the PU composite covering's surface and all-around dispersed FG. This improvement can be attributed to

the hydrophobic concept of the coatings, which reduces water cooperation and increases the pathway's convolution for the dispersion of harmful media. The majority of these components strengthen the ultimate FG/PU composite covering's defense against erosion. Transmission electron microscopy, examining electron microscopy, nuclear power microscopy, X-beam photoelectron spectrometry, Raman spectroscopy, Fourier change infrared spectroscopy, and other techniques were used to illustrate the main and morphological characteristics of the PU composite coatings. The coatings exhibited a unique round cone shape with distinct characteristics (widths of 8 µm distributed eight, six, and four µm apart, respectively).

## **Conclusions and Future Perspectives**

There has been a steady and robust increase in the need for materials based on polyurethane throughout time. Particle filters (PUs) are widely used as coatings to prevent corrosion on metals. A chance to include new green PU formulations was presented by the growing recognition on a worldwide scale of the significance of environmental and human health. As a result, there has been a lot of interest in the design and development of highly effective polyurethanes (PUs) that are less harmful to the environment than their conventional equivalents made from polyols and polyisocyanates derived from petroleum. The current research on the application of such green polyurethaneswaterborne and bio-based polyurethanes in particular—as protective coatings is gathered in this review.

Acknowledgments. The work was financially supported by the Ministry of Science and Education of the Republic of Kazakhstan, program-targeted financing out of competitive procedures for 2023– 2025. Project No. (BR21881822), entitled "Development of Technological Solutions for Optimizing Geological and Technical Operations When Drilling Wells and Oil Production at the Late Stage of Field Exploitation".

**Conflicts of interest.** The authors declare no conflict of interest.

*Cite this article as:* Yeligbayeva G, Khaldun MA, Abdassalam A Alfergani, Tleugaliyeva Zh, Karabayeva A, Bekbayeva L, Zhetpisbay DS, Shadin N.A., Atabekova Z. Polyurethane as a versatile polymer for coating and anti-corrosion applications: A review. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2024; 331(4):21-41. https://doi.org/10.31643/2024/6445.36

# Полиуретан қаптауға және коррозиядан қорғауға арналған универсалды полимер ретінде: Шолу

## <sup>1\*</sup>Елигбаева Г.Ж., <sup>2</sup>Халдун М.А., <sup>3</sup>Абдассалам А. Альфергани, <sup>4</sup>Тлеугалиева Ж.А., <sup>4</sup>Карабаева А. Е., <sup>1,5</sup>Бекбаева Л.К., <sup>6</sup>Жетписбай Д.Ш., <sup>7</sup>Шадин Н.А., <sup>1</sup>Атабекова З.Б.

<sup>1</sup>Сәтбаев университеті, Мұнай өнеркәсібі мектебі, Алматы, Қазақстан

<sup>2</sup>Фармакологиялық және диагностикалық зерттеу орталығы (PDRC), Амман университеті Әл Ахлия, Амман, 19328, Иордания <sup>3</sup>Химия бөлімі, білім беру факультеті, Сирт университеті, Сирт, Ливия

<sup>4</sup>Материалтану және жасыл технологиялар мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан

<sup>₅</sup> Химия және химиялық технология факультеті, әл-Фараби атындағы Қаз¥У, Алматы, Қазақстан

<sup>6</sup>С.Ж. Асфендияров атындағы ҚазҰМУ, Жалпы медицина мектебі, Алматы, Қазақстан

<sup>7</sup>Абай атындағы Қазақ ұлттық педагогикалық университеті, Жаратылыстану және география институты, Алматы, Қазақстан

### түйіндеме

Мақала келді: 23 қараша 2023 Сараптамадан өтті: 8 желтоқсан 2023 Қабылданды: 15 желтоқсан 2023	Полиуретанды материалдарды әзірлеу және технологиялық процестерді оңтайландыру қазіргі уақытта ауқымды зерттеулердің тақырыбы болып табылады. Полиуретан жоғары физика-химиялық және пайдалану қасиеттерімен сипатталады. Полиуритандар тозуға, майға және бензинге төзімді. Олар керемет жылу физикалық және созылғыш қасиеттерге ие. Бұл полиуретандарды жоғары эксплутациялық қасиеттері бар материалдарды қажет ететін көптеген салаларда қолдануға мүмкіндік береді. Полиуретандар сонымен қатар көптеген салаларда коррозияға қарсы агент ретінде қорғағыш жабындарын өндіруде кеңінен қолданылады. Полиуретанды полимерлердің физика-механикалық және экспуатациялық қасиеттерін, атап айтқанда модификацияланған полиуретанды жабындардың коррозияға қарсы қасиеттері жақсартуға арналған көптеген зерттеулер жүргізілді. Полиуретанды полимерлердің әртүрлі қолдануларға арналған қасиеттерін мономерлер мен олардың арақатынасын, сондай-ақ өндіріс процесінің өзін өзгерту арқылы жақсартуға болады. Полиолдар мен изоцианат мономерлеріне негізделген полиуретанды полимерлерді алу катализатордың қатысуымен полимерлеу процесіне де, толуол, ксилол және ацетон сияқты еріткіштерді қолдануға да негізделген. Әртүрлі әдістермен зерттелген полиуретанды полимерлердің физика-механикалық қасиеттеріне әсер ететін бірнеше факторлар бар. Мұңдай факторларға изоцианаттардың, полиолдардың түрлері, ОСИ/ОН қатынасы, еріткіштер, катализаторлар және температура жатады. Әдетге, полиолдар полиуретанды полимерлердің иілгіштігіне жауап береді, ал изоцианаттар полиуретанды полимердің қаттылығына және полимердің негізгі бөлігінің бірігуіне (тіглуіне) жауап береді. Реагенттердің химиялық құрамын өзгерту арқылы пайдалану мақсатына байланысты жабынның сипаттамалары өзгертіледі. Қорытынды әсер әртүрлі полиолдар мен полиизоцианаттардың химиялық құрамыне анықталады. Полиуретанды полимерлердің қарсо қасиеттер сияқты полиуретанды полимерлердің қасиеттері зерттелді. Нәтижесінде гидрофобтылық, ыстыққа төзімділік, кеханикалық және коррозияға қарсы қасиеттер сияқты полиуретанды ы солиу мат		
	<i>Түйін сөздер:</i> Полиуретан, жабын, коррозияға қарсы, полиолдар, полиизоцианаттар.		
Елигбаева Гульжахан Жакпаровна	Авторлар туралы ақпарат: Химия ғылымдарының докторы, профессор, Мұнай инженериясы кафедрасы, Сәтбаев университеті, Сәтбаев көшесі, 22, Алматы 050013, Қазақстан. Етаіl: g.yeligbayeva@satbayev.university		
Халдун М. Аль Аззам	Химия кафедрасы, Жаратылыстану ғылымдары мектебі, Иордания университеті, 11942, Амман, Иордания. Email: azzamkha@yahoo.com		
Абдассалам А. Альфергани	Химия бөлімі, білім беру факультеті, Сирт университеті, Сирт, Ливия. Email: abdassalamtameem@yahoo.com		
Тлеугалиева Жанетта Асхатовна	Материалтану және жасыл технологиялар мектебі, Қазақстан-Британ Техникалық Университеті Төле би көшесі, 59, 050000, Алматы, Қазақстан. Email: z_tleugalieva@kbtu.kz		
Карабаева Айкүміс Ермекқызы	Материалтану және жасыл технологиялар мектебі, Қазақстан-Британ Техникалық Университеті Төле би көшесі, 59, 050000, Алматы, Қазақстан. Етаіl: a_karabayeva@kbtu.kz		
Бекбаева Ляззат	Ұлттық ашық нанотехнология зертханасы, ҚазҰУ. Әл-Фараби, әл-Фараби даңғылы, 050040, Алматы, Қазақстан Республикасы. Етаіl: lyazzat_bk2019@mail.ru		
Жетписбай Д.Ш.	С.Ж. Асфендияров атындағы ҚазҰМУ, Жалпы Медицина Мектебі 1, Биохимия кафедрасы, 480012, Төле би көшесі, 88, Алматы, Қазақстан. Email: zhetpisbay.d@kaznmu.kz		
Шадин Н.А.	Абай атындағы Қазақ Ұлттық Педагогикалық Университеті, Жаратылыстану және география институты, Химия кафедрасы, Қазыбек би көшесі, 30, Алматы, Қазақстан. Email: nugen_87@mail.ru		
Атабекова 3.Б.	Сәтбаев университеті, Мұнай инженериясы кафедрасы, Инженер. Email: zau888@mail.ru		

# Полиуретан как универсальный полимер для нанесения покрытий и защиты от коррозии: Обзор

<sup>1\*</sup>Елигбаева Г.Ж., <sup>2</sup>Халдун М.А., <sup>3</sup>Абдассалам А. Альфергани, <sup>4</sup>Тлеугалиева Ж.А., <sup>4</sup>Карабаева А. Е., <sup>1,5</sup>Бекбаева Л.К., <sup>6</sup>Жетписбай Д.Ш., <sup>7</sup>Шадин Н.А., <sup>1</sup>Атабекова З.Б.

<sup>1</sup>Сатбаев Университет, Кафедра Нефтяной Инженерии, Алматы, Казахстан

<sup>2</sup>Центр фармакологических и диагностических исследований (PDRC), Амманский университет Аль-Ахлия, Амман, 19328, Иордания <sup>3</sup>Кафедра химии, педагогический факультет, Университет Сирта, Сирт, Ливия

<sup>4</sup> Факультет материаловедения и зеленых технологий, Казахстанско-Британский технический университет, Алматы, Казахстан <sup>5</sup> Факультет химии и химической технологии КазНУ им. Аль-Фараби, Алматы, Казахстан

<sup>6</sup> КазНМУ им. Асфендиярова, лечебный факультет, Алматы, Казахстан

<sup>7</sup>Казахский национальный педагогический университет имени Абая, Институт естественных наук и географии, Алматы, Казахстан

#### Аннотация

Разработка полиуретановых материалов и оптимизация технологических процессов в настоящее время являются предметом общирных исследований. Полиуретан характеризуется высокими физико-химическими и эксплуатационными свойствами. Полиуританы обладают высокой износостойкостью, масло- и бензостойкостью. Они имеют прекрасными теплофизические и эластичные свойства. Это позволяет применять полиуретаны во многих отраслях промышленности, где требуются материалы с высокими эксплуатационными свойствами. Полиуретаны также широко используются во многих отраслях промышленности при производстве защитных покрытий в качестве антикоррозийных средств. Было проведено значительное количество исследований, посвященных улучшению физико-механических и эксплуатационных свойств полиуретановых полимеров, в частности антикоррозийных свойств модифицированных полиуретановых покрытий. Свойства полиуретановых полимеров для различных применений могут быть улучшены путем изменения используемых мономеров и их Поступила: 23 ноября 2023 соотношений, а также самого процесса получения. Получение полиуретановых полимеров Рецензирование: 8 декабря 2023 на основе полиолов и изоцианатных мономеров основано как на процессе Принята в печать: 15 декабря 2023 полиприсоединения в присутствии катализатора, так и применении растворителей, таких как толуол, ксилол и ацетон. Существуют различные факторы, влияющие на физикомеханические свойства полиуретановых полимеров, которые были исследованы различными методами. Такими факторами были типы изоцианатов, полиолов, соотношения ОСN/OH, растворители, катализаторы и температуры. Как правило, полиолы отвечают за гибкость полиуретановых полимеров, а изоцианаты отвечают за жесткость полиуретанового полимера и сшивку между основной частью полимера. Благодаря гибкому изменению химического состава реагентов они могут изменять характеристики покрытия в зависимости от предполагаемого использования. Конечный эффект определяется химическим составом различных полиолов и полиизоцианатов. Были исследованы гидрофобность. термостойкость, механические и антикоррозийные свойства полиуретановых полимеров. Как результат, свойства полиуретановых полимеров, такие как гидрофобность, термостойкость, механические и антикоррозийные свойства, улучшились под воздействием вышеперечисленных факторов. В этой обзорной статье дается краткое описание наиболее современных, финансово успешных методов создания защитных полиуретановых покрытий и использования их в качестве антикоррозийных средств. Ключевые слова: Полиуретан, покрытие, антикоррозийное, полиолы, полиизоцианаты. Информация об авторах: Доктор химических наук, профессор, Кафедра Нефтяной Инженерии, Сатбаев Елигбаева Гульжахан Жакпаровна Университет, ул. Сатбаева, 22, 050013, Алматы, Казахстан. Email: g.yeligbayeva@satbayev.university Кафедра химии, Школа естественных наук, Иорданский университет, 11942, Амман, Халдун М. Аль Аззам Иордания. Email: azzamkha@yahoo.com Химический факультет, педагогический факультет, Сиртский университет, Сирт, Абдассалам А. Альфергани Ливия. Email: abdassalamtameem@yahoo.com Школа материаловедения и зеленых технологий, Казахстанско-Британский технический Тлеугалиева Жанетта Асхатовна университет, ул. Толе би, 59, 050000, Алматы, Казахстан. Email: z tleuqalieva@kbtu.kz Школа материаловедения и зеленых технологий, Казахстанско-Британский технический Карабаева Айкумис Ермеккызы университет, ул. Толе би, 59, 050000, Алматы, Казахстан. Email: a\_karabayeva@kbtu.kz Национальная открытая лаборатория нанотехнологий. КазНУ им. Аль-Фараби. пр. Аль-Бекбаева Ляззат Фараби, 050040, Алматы, Казахстан. Email: lyazzat\_bk2019@mail.ru Кафедра биохимии, Школа Общей Медицины, КазНМУ имени С.Д. Асфендиярова, 480012, Жетписбай Д.Ш. ул. Толе би, 88, Алматы, Казахстан. Email: zhetpisbay.d@kaznmu.kz Кафедра Химия, Институт естествознания и географии, Казахский Национальный Шадин Н.А. Педагогический Университет имени Абая, ул.Казыбек би, 30, Алматы, Казахстан. nugen\_87@mail.ru Атабекова З.Б. Школа Нефтяной Инженерии, Сатбаев Университет. Инженер. Email: zau888@mail.ru

### References

[1] Petrovic ZS, DooPyo H, Javn I, Erina N, Zhang F, Ilavsky J. Phase structure in segmented polyurethanes having fatty acidbased soft segment. Polymer. 2013; 54:372-380.

[2] Diego Piazza, Debora S Silviera, Natalia P Lorandi. Polyester-based powder coatings with montmorillonit nanoparticle applied carbon steel. Progress in organic Coatings. 2012; 73:42-46.

[3] Petrovic ZS, Cevallos MJ, Javni I, Schaefer DW, Justice R. Journal of Polymer Science, Part B: Polymer Physics. 2005; 43(22):3178-3190.

[4] Velayutham TS, Abd Majid WH, Ahmad AB, Kang GY, Gan SN. Progress in Organic Coatings. 2009; 66:367-371.

[5] Suhreta Husic, Ivan Javni, Zoran S. Petrovic. Composites Science and Technology. 2005; 65:19-25.

[6] Wicks ZW, Jones PN, Pappas SP. Organic Coatings: Science and Technology. 2nd edition, John Wiley & Sons. Inc.: New York. 1999, 630.

[7] Ingold CK. Structure and Mechanism in Organic Chemistry. 2nd edition, Cornell University Press: Ithaca, New York. 1969, 1129-113.

[8] Das A, Mahanwar P. A brief discussion on advances in polyurethane applications. Adv. Ind. Eng. Polym. Res. 2020; 3:93-101.

[9] Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR. Polyurethane types, synthesis and applications. A review. RSC Adv. 2016; 6:114453-114482.

[10] Yuan Y, Lee TR. Contact Angle and Wetting Properties. In Surface Science Techniques; Springer: Berlin-Heidelberg, Germany. 2013, 3-34.

[11] Oertel G, Abele L. Polyurethane Handbook: Chemistry, Raw Materials, Processing, Application, Properties. Hanser Publishers. Distributed in USA By Scientific and Technical Books, Macmillan. 1985, 688.

[12] Da-Kong Lee, Hong-Bing Tsai. Properties of segmented PUR derived from different diisocyanatos. Journal of Applied Polymer Science. 2000; 75(1):167-174.

[13] Caraculacu AA, Coseri S. Isocyanates in polyaddition processes. Structure and reaction mechanisms. Progress in Polymer Science. 2001; 26:799-851.

[14] Ionescu M. Chemistry and Technology of Polyols for Polyurethanes. Rapra Publishing. 2005, 392.

[15] Ferrer MCC, Babb D, Ryan AJ. Characterization of polyurethane networks based on vegetable derived polyol . Polymer. 2008; 49(15):3279-3287.

[16] Szycher M. Szycher 's handbook of polyurethanes. CRC Press: Florida. 1999, 1112.

[17] Zhang C, Dai X, Wang Y, Sun G, Li P, Qu L, Sui Y, Dou Y. Preparation and corrosion resistance of ETEO modified graphene oxide/epoxy resin coating. Coatings. 2019; 9:46.

[18] Hepburn C. Polyurethane elastomers. Elsevier Applied Science. 1992, 441.

[19] Patent 6423816. US. Polyester polyols and their use as a binder component in two-component polyurethane coating composition. Wamprecht C, Sonntag M. 2002.

[20] Patent 6184332. US. Polyester polyols and their use as the polyol component in two-component polyurethane paints. Santos D, Manuel A. 2001.

[21] Patent 6809172. US. Polyester polyols and the use of polyester for producing polyurethane cast elastomers that have an improved resistance to hydrolysis. Barnes JM, Schneider M, Hoffmann A. 2004.

[22] Velankar S, Cooper SL. Microphase Separation and Rheological Properties of Polyurethane Melts. 1. Effect of Block Length. Macromolecules. 1998; 31:9181-9192.

[23] Korley LTJ, Pate BD, Thomas EL, Hammond PT. Effect of the Degree of Soft and Hard Segment Ordering on the Morphologyand Mechanical Behavior of Semicrystalline Segmented Polyurethanes. Polymer. 2006; 47:3073-3082.

[24] Matthew A. Hood, Bingbing Wang, James M Sands, John J La Scala, Frederick L Beyer, Christopher Y Li. Morphology control of segmented polyurethanes by crystallization of hard and soft segments. Polymer. 2020; 51(10):2191-2198.

[25] Yan Wu, Kuiling Wei, Yinglin Zhang, Chengcheng Miao. Fabrication of self-replenishing hydrophobic surfaces and selfcleaning coating based on self-crosslinkable PDMS-g-WPU emulsion. Progress in Organic Coatings. 2023; 175:107375.

[26] Ismail Eid A, Motawie AM, Sadek EM. Synthesis and characterization of polyurethane coatings based on soybean oil–polyester polyols. Egyptian Journal of Petroleum. 2011; 20(2):1-8.

[27] Velayutham TS, Abd Majid WH, Ahmad AB, Gan Yik Kang, Gan SN. Synthesis and characterization of polyurethane coatings

derived from polyols synthesized with glycerol, phthalic anhydride and oleic acid. Progress in Organic Coatings. 2009; 66(4):367-371. [28] Velayutham TS, Abd Majid WH, Ahmad AB, Yik KG, Seng NG. The physical and mechanical properties of polyurethanes from oleic acid polyols. Journal of Applied Polymer Science. 2009; 112(6):3554-3559.

[29] Ranjeet BD, Pavan MP, Yogeshsing NR, Ravindra DK. Synthesis and characterization of gree polyurethane coatings derived from Niger-seed-oil-based polyester amide polyols. European Journal of Lipid Science and Technology. 2002; 124(2):2100171.

[30] Rudlong AM, Goddard JM. Synthesis and Characterization of Hydrophobic and Low Surface Tension Polyurethane. Coatings. 2023; 13(7):1133.

[31] Kim TH, Kim M, Lee W, Kim H-G, Lim C-S, Seo B. Synthesis and Characterization of a Polyurethane Phase Separated to Nano Size in an Epoxy Polymer. Coatings. 2019; 9(5):319.

[32] Zaimahwati, Yuniati, Jalal R, Rihayat T, Zhafiri S. Synthesis and characterization thermal of polyurethane. MMT from Castrol oil polyols for coating. Conf. Ser.: Mater. Sci. Eng. 2019; 536:012037.

[33] Yilgor I, Yilgor E Polym. Structure-morphology-property behavior of segmented thermoplastic polyurethanes and polyureas prepared without chain extenders. Polymer Reviews. 2007; 47:487-510.

[34] Yeh F, Hsiao BS, Sauer BB, Michel S, Siesler HW. Preparation, characterization and properties of novel bisphenol-A type novolac epoxy-polyurethane polymer with high thermal stability. Macromolecules. 2003; 36:1940.

[35] Garrett JT, Runt J, Lin JS. Compression-molded polyurethane block copolymers. Evaluation of microphase compositions. Macromolecules. 2000; 33:6353.

[36] Kausar A, Zulfiqar S, Sarwar MI. High performance segmented polyurethanes derived from a new aromatic diisocyanate and polyol. Polym. Degrad. Stab. 2013;98(1):368-686.

[37] Mara CL, Renato AA, Isolda C. Effect of the NCO/OH Molar Ratio on the Physical Aging and on the Electrochemical Behavior of Polyurethane-Urea Hybrid Coating. Int. J. Electrochem. Sci. 2013; 8:4679-4689.

[38] Mishra AK, Narayan R, Raju KVSN, Aminabhavi TM. Hyperbranched polyurethane (HBPU)-urea and HBPU-imide coatings: effect of chain extender and NCO/OH ratio on their properties. Prog Org Coat. 2012; 74:134-141.

[39] Negim E-SM, Bekbayeva L, Mun GA, Abilov ZA, Saleh MI. Effects of NCO/OH ratios on physico-mechanical properties of polyurethane dispersion. World Appl. Sci. J. 2011; 14:402.

[40] García-Pacios V, Costa V, Colera M, Martín-Martínez JM. Waterborne polyurethane dispersions obtained with polycarbonate of hexanediol intended for use as coatings. Prog. Org. Coat. 2011; 71:136-146.

[41] Hongmei J, Zhen Z, Wenhui S, Xinling W. Inc. Moisture-cured polyurethane/polysiloxane copolymers: Effects of the structure of polyester diol and NCO/OH ratio. J Appl Polym Sci. 2008; 108(6):3644-3651.

[42] Prabhakar A, Chattopadhyay DK, Jagadeesh, Raju KVSN. Structural investigations of polypropylene glycol; (PPG) and isochrone diisocyanate (IPDI)-based polyurethane prepolymer by 1D and 2D NMR spectroscopy. Journal of Polymer Science. Part A: Polymer Chemistry. 2005; 43(6):1196-1209.

[43] Semsarzadeh MA, Navarchian AH. Effects of NCO/OH ratio and catalyst concentration on structure, thermal stability, and crosslink density of poly(urethane-isocyanurate). Journal of Applied Polymer Sci. 2003; 90(4):963-972.

[44] Runumi G, Utpal KN, Sarwar MA, Dayal SM. Study of Effect of NCO/OH Molar Ratio and Molecular Weight of Polyol on the Physico-Mechanical Properties of Polyurethane Plaster Cast. World Applied Sciences Journal. 2013; 21(2):276-283.

[45] Kewen Cai, Shixiang Zuo, Shipin Luo, Chao Yao, Wenjie Liu, Jianfeng Ma, Huihui Mao and Zhongyu Li. Preparation of polyaniline/graphene composites with excellent anti-corrosion properties and their application in waterborne polyurethane anticorrosive coatings. RSC Advances. 2016, 98.

[46] Youtong Wu, Shaoguo Wen, Kaiming Chen, Jihu Wang, Guangyu Wang, Kai Sun. Preparation of sulfonated graphene/zinc phosphate mixtures as anti-corrosion additives in the aqua polyurethane tar. Progress in Organic Coatings. 2019; 132:409-416.

[47] Gan Cui, Zhenxiao Bia, Shuaihua Wang, Jianguo Liu, Xiao Xing, Zili Li, Bingying Wang. A comprehensive review on smart anti-corrosive coatings. Progress in Organic Coatings. 2020; 148:105821.

[48] Pei-Ying Tsai, Tzu-En Chen and Yueh-Lien Lee. Development and Characterization of Anticorrosion and Antifriction Properties for High Performance Polyurethane/Graphene Composite Coatings. Coatings. 2018; 7:250.

[49] To Thi Xuan Hang, Ngo Thanh Dung, Trinh Anh Truc, Nguyen Thuy Duong, Bui Van Truoc, Pham Gia Vu, Thai Hoang, Dinh Thi Mai Thanh, Marie-Georges Olivier. Effect of silane modified nano ZnO on UV degradation of polyurethane coatings. Progress in Organic Coatings. 2015; 79:68-74.

[50] Huibin Zhu, Weihong Hu, Sipei Zhao, Xin Zhang, Li Pei, Guizhe Zhao, and Zhi Wang. Flexible and thermally stable superhydrophobic surface with excellent anti-corrosion behavior. Journal of Materials Science. 2020; 55:2215-2225.

[51] Yao Tong, Siva Bohm, Mo Song. The capability of graphene on improving the electrical conductivity and anti-corrosion properties of Polyurethane coatings. Applied Surface Science. 2017; 424:72-81.

[52] Mahmudzadeh M, Yari H, Ramezanzadeh B, Mahdavian M. Urtica dioica extract as a facile green reductant of graphene oxide for UV resistant and corrosion protective polyurethane coating fabrication. Journal of Industrial and Engineering Chemistry. 2019; 78:125-136.

[53] Xiaoyun Yea, Zhaopeng Wanga, Lian Maa, Qianting Wanga, Anni Chua. Zinc oxide array/polyurethane nanocomposite coating: fabrication, characterization and corrosion resistance. Surface and Coatings Technology. 2019; 358:497-504.

[54] Hui Wang, Junhuai Xu, Xiaosheng Du, Zongliang Du, Xu Cheng, Haibo Wang. A self-healing a polyurethane-based composite coating with high strength and anti-corrosion properties for metal protection. Composites. Part B: Engineering. 2021; 225:109273.

[55] Godinho B, Gama N, Barros-Timmons A, Ferreira A. Recycling of different types of polyurethane foam wastes via acidolysis to produce polyurethane coatings. Sustainable Materials and technology. 2021; 29.

[56] Hui Yuan, Yushuai Wang, Zhiyong Liu and Shiyu Li. A study on the properties and working mechanism of a waterborne polyurethane-modified silicatebased coating. RSC (Royal Society of Chemistry) Adv. 2019; 9:26817-26824.

[57] Fengyuan Zhanga, Weiqu Liua, Liyan Lianga, Maiping Yanga, Shuo Wanga, Hongyi Shia, Yankun Xiea, Ke Pia. Application of polyether amine intercalated graphene oxide as filler for enhancing hydrophobicity, thermal stability, mechanical and anti-corrosion properties of waterborne polyurethane. Diamond and Related Materials. 2020; 109:108077.

[58] Jiahua Zhu, Suying Wei, Ian Y Lee, Sung Park, John Willis, Neel Haldolaarachchige, David P. Young Zhiping Luo and Zhanhu Guo. Silica stabilized iron particles toward anti-corrosion magnetic polyurethane nanocomposites. RSC Advances. 2012; 2:1136-1143.

[59] Tuan Syarifah Rossyidah Tuan Naiwi, Min Min Aung, Marwah Rayung, Azizan Ahmad, Kai Ling Chai, Mark Lee Wun Fui, Emma Ziezie Mohd Tarmizi, Nor Azah Abdul Aziz. Dielectric and ionic transport properties of bio-based polyurethane acrylate solid polymer electrolyte for application in electrochemical devices. Polymer Testing. 2022; 106:107459.

[60] Cheng Zhang, Kuan-Chen Huang, Haoran Wang, Qixin Zhou. Anti-corrosion non-isocyanate polyurethane polysiloxane organic/inorganic hybrid coatings. Progress in Organic Coatings. 2020; 148:105855.

[61] Pavan M Paraskar, Mayur S Prabhudesai, Vinod M Hatkar, Ravindra D Kulkarni. Vegetable oil-based polyurethane coatings. Progress in Organic Coatings. 2021; 156:106267.

[62] Aqdas Noreen, Khalid Mahmood Zia, Mohammad Zuber, Shazia Tabasum, and Muhammad Jawwad Saif. Recent trends in environmentally friendly water-borne polyurethane coatings: A review. Korean Journal of Chemical Engineering. 2015; 33:388-400.

[63] Jing Li, Jincan Cui, Jiayun Yang, Yaya Li, Hanxum Qui, Junhe Yang. Reinforcement of graphene and its derivatives on the anticorrosive properties of waterborne polyurethane coatings. Composites Science and Technologyю. 2016; 129:30-37.

[64] Ashraf M El Saeed, M Abd El-Fattah, Ahmed M Azzam. Synthesis of ZnO nanoparticles and studying its influence on the antimicrobial, anticorrosion and mechanical behavior of polyurethane composite for surface coating. Dyes and Pigments. 2015; 121:282-289.

[65] Pooneh Haghdadeh, Mehdi Ghaffari, Bahram Ramezanzadehb, Ghasem Bahlakeh, Mohammad Reza Sae. The role of functionalized graphene oxide on the mechanical and anti-corrosion properties of polyurethane coating. Journal of the Taiwan Institute of Chemical Engineers. 2018; 86:199-212.

[66] Abhijit Das, Prakash Mahanwar. A brief discussion on advances in polyurethane applications. Advanced Industrial and Engineering Polymer Research. 2020; 3:93-101.

[67] Xiaohua Konga, Guoguang Liua, Hong Qi, Jonathan M Curtis. Preparation and characterization of high-solid polyurethane coating systems based on vegetable oil derived polyols. Progress in Organic Coatings. 2013; 76:1151-1160.

[68] Ewa A Papaj, Douglas J Mills, Sina S Jamali. Effect of hardener variation on protective properties of polyurethane coating. Progress in Organic Coatings. 2014; 77:2086-2090.

[69] Mandar S Gaikwada, Vikas V Gitea, Pramod P Mahulikar, Dilip G Hundiwalea, Omprakash S Yemul. Eco-friendly polyurethane coatings from cottonseed and karanja oil. Progress in Organic Coatings. 2015; 86:164-172.

[70] Tsao-Cheng Huang, Guan-Hui Laia, Chen-En Li, Mei-Hui Tsai, Peng-Yun Wan, Yi-Hsiu Chung, Meng-Hung Lin. Advanced anticorrosion coatings prepared from  $\alpha$ -zirconium phosphate/polyurethane nanocomposites. RSC Advances. 2017; 7:9908-9913.

[71] Ying Liang, Dong Zhang, Mengyu Zhou, Yuzheng Xia, Xiaonong Chen, Susan Oliver, Shuxian Shi, Lei Lei. Bio-based omniphobic polyurethane coating providing anti-smudge and anti-corrosion protection. Progress in Organic Coatings. 2020; 148:105844.

[72] Xiuyong Chen, Jianhui Yuan, Jing Huang, Kun Ren, Yi Liu, Shaoyang Lu, Hua Li. Large-scale fabrication of superhydrophobic polyurethane/nano-Al2O3 coatings by suspension flame spraying for anti-corrosion applications. Applied Surface Science. 2014; 311:864-869.

[73] Yajun Wang, Guoyue Xu, Huijuan Yu, Chen Hu, Xiaoxing Yan, Tengchao Guo, Jiufen Li. Comparison of anti-corrosion properties of polyurethane based composite coatings with low infrared emissivity. Applied Surface Science. 2011; 257:4743-4748.

[74] Xia Wang, Jiaojiao Hu, Ying Li, Jinrui Zhang, Yuanyuan Ding. The surface properties and corrosion resistance of fluorinated polyurethane coatings. Journal of Fluorine Chemistry. 2015; 176:14-19.

[75] Anna M Mikhailova, Moussa Tamboura, Meng Qiu Jia. Heat-Resistant and Anti-Corrosion Urethane-Silicone-based Coatings. Silicon. 2012; 4:197-208.

[76] Yixing Zeng, Hongqiang Li, Jian Li, Jinxin Yang, Zhonghua Chen. Preparation and characterization of solvent-free anticorrosion polyurethane-urea coatings. Surfaces and Interfaces. 2023, 36.

[77] Mengting Moa, Wenjie Zhao, Zifei Chena, Eryong Liu, Qunji Xue. Corrosion inhibition of functional graphene reinforced polyurethane nanocomposite coatings with regular textures. RSC Advances. 2016; 6:7780-7790.