Polyurethane Classification, Properties, Synthesis, and Application- A Review

Israa K. Mohammed, Leqaa A. Mohammed, Omar G. Hammoodi[*], Department of Chemistry, College of Science, University of Diyala
Mustafa A. Alheety, Department of Nursing, Al-Hadi University
Abdulwahhab H. Majeed, Department of Chemistry, College of Science, University of Diyala
israak@uodinyala.edu.iq
Liqaaadnan@uodinyala.edu.iq
omerkazi@uodiyala.edu.iq
Mustafa1990alhcety@gmail.com
abdulwahnab@uodinyala.edu.iq

Abstract:
Polyurethane is a synthetic polymer with a wide range of applications due to its unique structure and properties. This review highlights the chemistry of polyurethane and its several types. Polyurethanes are classified according to their chemical structure into polyether polyurethanes and polyester polyurethanes. Polyurethanes are also classified according to their shape into flexible polyurethanes and rigid polyurethanes. These polymers are produced by the reaction of polyisocyanates and polyols, and other additives are also added during their preparation, including catalysts, chain extenders and crosslinkers, surfactants, and blowing agents. The physical and chemical properties of polyurethanes have given them numerous industrial applications, including (coatings, adhesives, sealants, plastics, automotive, medical, textiles and apparels, marine, and wood-based polyurethane composites.

Keywords: Polyurethane, polyisocyanates, polyols and plastics).

البولي يوريثان: تصنيفه وخصائصه وطرق تحضيره وتطبيقاته – مراجعة

اسراء خاجي محمد، لقاء عدنان محمد: قسم الكيمياء- كلية العلوم- جامعة ديالى
عمر غازي حمودي
مصطفى عبدالغفور الهيتي: قسم التمريض- جامعة الهادي
عبدالوهاب حميد مجيد: قسم الكيمياء- كلية العلوم- جامعة ديالى

الخلاصة :

البولي يوريثان هو بوليمر صناعي ذو استخدامات واسعة النطاق بسبب بنيته وخصائصه المتميزة. هذه المراجعة تلقي الضوء على كيمياء البولي يوريثان وأنواعه المختلفة. حيث يصنف البولي يوريثان حسب التركيب الكيميائي إلى بولي إيثر بولي يورثان وبولي استر بولي يوريثان ويصنف البولي يوريثان أيضاً حسب الشكل إلى بولي يوريثان المرن والبولي يوريثان الصلب. تنتج هذه البوليمرات من تفاعل البولي آيزوسيانات والبوليولات وتضاف أيضاً مواد أخرى في التحضير منها العوامل المساعدة، موسعات السلسلة والروابط المتقاطعة، ومواد خافضة للشد السطحي، والعوامل النافخة. منحت الخصائص الفيزيائية والكيميائية للبولي يوريثان تطبيقات صناعية متعددة من أبرزها(الطلاءات، المواد اللاصقة، والمواد المانعة للتسرب، اللدائن، السيارات، الطبية، المنسوجات والملابس، الصناعات البحرية، ومركبات البولي يوريثان الخشبية).

الكلمات المفتاحية: البولي يوريثان ، تصنيف البولي يوريثان ، خصائص البولي يوريثان ، تحضير البولي يوريثان .

1. Introduction:

Polyurethanes are materials that are widely employed in many different applications. Polyurethanes, sometimes known as urethanes, are also written as PUR or PU. Their urethane bond (-NH-CO-O-) is what distinguishes them. In 1937, Otto von Baeyer and associates made

---

[*] Corresponding author : Omar G. Hammoodi .

the discovery of polyurethanes at the I.G. Farben laboratory in Leverkusen, Germany [1–5]. The characteristic structure of urethanes is shown as:

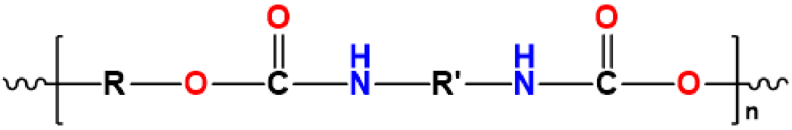


Figure 1. structure of polyurethanes [2].

Polyurethane research has advanced significantly over the past few decades, with research focusing on whether polyurethanes are biostable or biodegradable form. They have been used in a variety of applications, including functional medical devices, drug delivery systems, tissue engineering structure, and more. Polyurethanes are currently one of the most versatile materials in the world. These days, polyurethane may be found in many different applications, such as stiff foam for walls, flexible foam for upholstered furniture, thermoplastic polyurethane for footwater and medical gadgets, adhesives, coatings, sealants, and synthetic rubber for floors and car interiors [6,7]. Over the past 30 years, polyurethanes have become more widely used in a wide range of applications due to their comfort, affordability, energy efficiency, and possible environmental friendliness. What are some of the reasons polyurethanes are so popular? The lifespan of various goods is influenced by the resilience of polyurethanes. This quality is an important environmental consideration that often favors the choice of polyurethane. Due to its cost-effectiveness, convenience, environmental friendliness, energy saving, polyurethane has seen its use increase over the past 30 years in a variety of applications, what are some of the factors that make polyurethane so desirable? Polyurethane's durability significantly contributes to the longevity of many products. This quality is an important environmental factor that favors the choice of polyurethane [8-10].

2. Classification of Polyurethanes:

2.1. Classification by Chemical Composition:

a- polyester urethane (ester-type PUR):

Ester polyurethane was developed in the 1940s. Due to its flexible and soft properties [11], it is primarily used in clothing, However, ester polyurethane is a biodegradable plastic due to the presence of ester bonds that degrade when exposed to microbial attack. Therefore, it is unstable [11-14]. To degrade ester PUR, several microorganisms that degrade it have been isolated, and the degradation mechanisms have been analyzed [15-17]. Therefore, ester PUR has recently been defined as a biodegradable plastic [18,19].

b- **Polyether Urethane (ether-type PUR):**

PEU is recognized by its poyether polyol repeat unit with good spinnability and low cohesive energy, due to presence of polyether diol in its soft segment. This gives PEU good flexibility at low temperature and excellent resistance to hydrolysis [20].

2.2. Classification by shape and structure

There are two varieties of polyurethane foam: stiff foam and flexible foam. Based on their intended use, these foams are further separated into several categories. The right isocyanate and polyol components are used to synthesize all types of polyurethane foams [2].

a- Flexible polyurethane foam:

Flexible polyurethane foams are made by slab stock or molding. They are classified based on the polyol base production method. Slab stock polyurethane foam, also known as viscoelastic foam, high-resilience foam, energy-absorbing foam, super-soft foam, polyether foam, and flexible polyester foam are among its several varieties. Hot-formed foam and cold-molded foam are the two categories of molded foam [2,22-29].

b- Rigid polyurethane foam:

Rigid polyurethane foam consists of a closed-cell structure. At room temperature, the production of rigid foam requires no heating. This type of foam has differing density values. Unique processes are utilize to manufacture this type of foam, such as single-component foam and spray foam. Rigid foam is further classified into laminates, sandwich panels, slab stock rigid foam, and high-density rigid foam [2,21]. Cup foam may also be used to create stiff and flexible foam on a lab size [30].

3. Synthesis of Polyurethanes:

Polyurethane is produced in several ways [31], the best of which is through the reaction of polyol and diisocyanate [32-34], as shown in Figure 2. Some materials can also be added as catalysts to produce polyurethane, such as pigments, fillers, flame retardants, cross-linkers, surfactants, and blowing agents. When the quantity of the materials used in the preparation change, the properties of the typical polyurethane vary, as shown in **Table 1**.

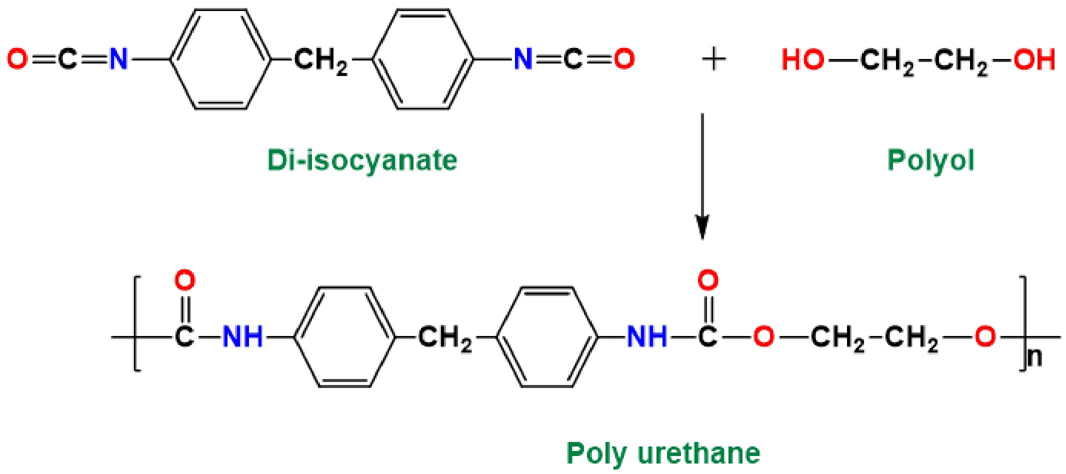


Figure 2: Synthesis of a typical PU.

Table 1: Variation of polyurethane properties with material quantities

Material Component	Concentration Range (%)	Primary Effect on Properties	Secondary Influences
Diisocyanate	35-55	Mechanical strength and rigidity	Thermal stability, chemical resistance
Polyol	40-65	Flexibility and elasticity	Processing characteristics, adhesion
Catalyst	0.05-1.5	Reaction kinetics	Cell structure, cure profile
Surfactant	0.2-2.5	Foam stability and cell structure	Surface characteristics
Blowing Agent	0.5-8	Density and insulation	Dimensional stability
Flame Retardant	5-25	Fire resistance	Mechanical properties, processing

3.1. Isocyanate:

Isocyanates are a functional group with the general formula N=C=O–, and are an isomer of the cyanate group, with the general formula O–C≡N–. The isocyanate group consists of a nitrogen atom double-bonded to a carbon atom, which in turn is double-bonded to an oxygen atom. The organic residue R, via nitrogen readily bonds with amines, water, thiols, alcohols, urea groups, urethanes, epoxides, carboxylic acids, and cyclic anhydrides, or self-reacts with other isocyanates [35,36] as shown in **Figure 3**. The effectiveness of isocyanates in reacting with hydrogen-bonded groups explains their widespread use in polyurethane chemistry.

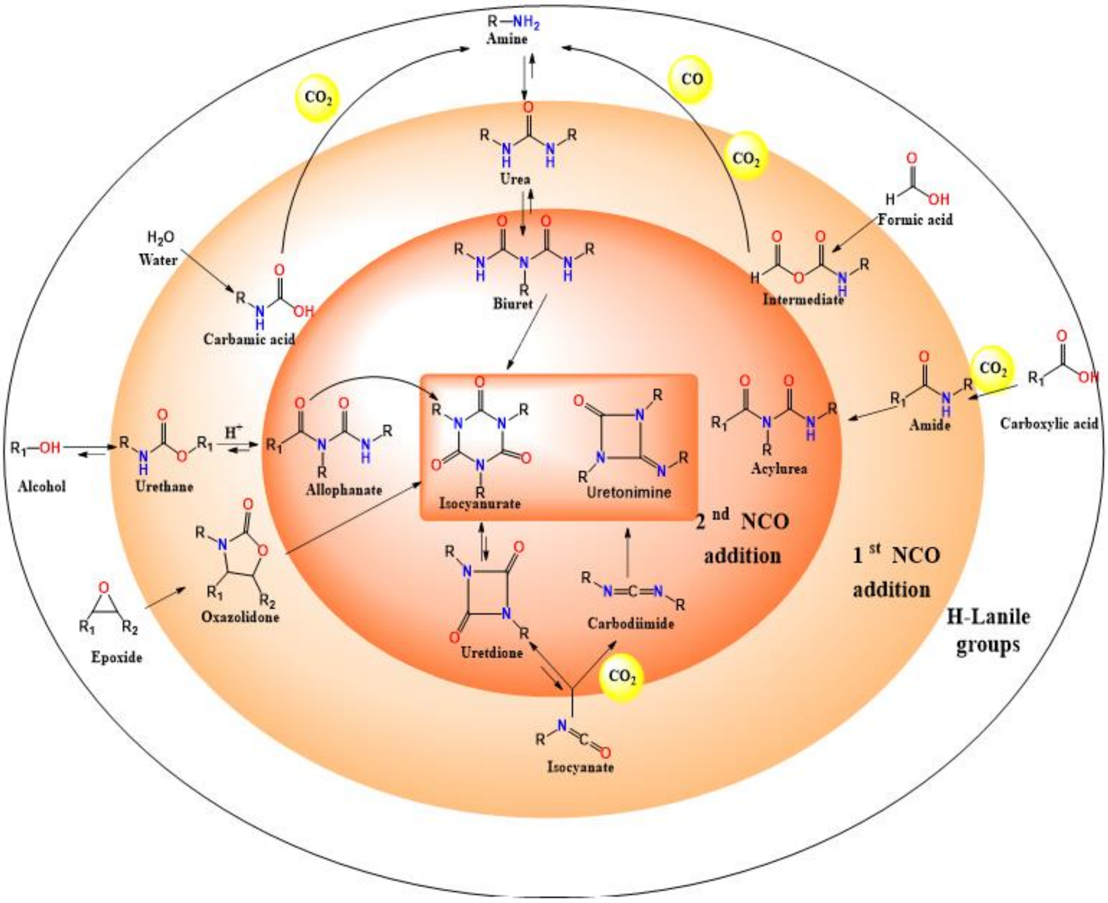
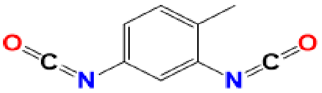
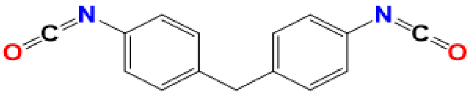
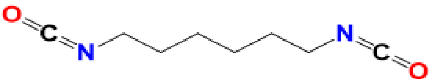
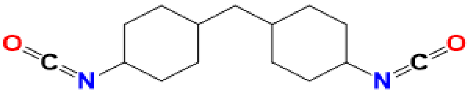
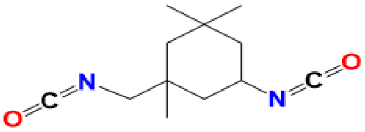


Figure 3: An overview of the primary chemical reactions that occur between hydrogen and isocyanate groups, taken from [37].

The structural properties of polyisocyanate compounds might be polycyclic, cycloaliphatic, aromatic, or aliphatic. The following are the main diisocyanate molecules used in PU chemistry: Commercially available as mixtures of 2,4 and 2,6 isomeric forms are (i) 1,6-hexamethylene diisocyanate (HDI), (ii) toluene diisocyanate (TDI), (iii) 4,4'-methylenediphenyl diisocyanate (MDI) and polymeric 4,4'-MDI (pMDI), (iv) 4,4'-dicyclohexyl diisocyanate (HMDI), and (v) isophorone diisocyanate (IPDI). **Table 2** presents their molecular structures. Except for pMDI, which has an average functionality of 2.7, all these polyisocyanates compounds display bifunctional properties. They are also all produced using phosgene-based chemistry and are obtained from petroleum [38,39]. Aromatic diisocyanate compounds such as TDI and MDI constitute approximately 95% of the diisocyanate marketplace due to the accessibility and economic advantages of aromatic diamine precursors [40]. The electron delocalization within the aromatic ring systems of isocyanate compounds enhances their effectiveness [41]. The stability characteristics of aromatic isocyanate compounds result in improved thermal properties and flame-resistant characteristics. Aliphatic isocyanate compounds provide advantages for UV resistance and oxidation stability [42]. In symmetric diisocyanate molecules, both NCO functionalities exhibit equivalent reactivity. However, the reactivity of the remaining unreacted NCO group decreases once a nucleophilic molecule is added to one isocyanate group to form the first urethane connection. This process is caused by the produced urethane group's electron-donating impact [40,43,44]. The first isocyanate functions of MDI and HDI, for example, show reactivity that is 2.9 and 2.0 times higher than that of the second functionality, respectively. With asymmetric diisocyanate molecules, this reactivity difference is more noticeable. For instance, the first OH group added to 2,4-TDI is incorporated twelve times faster than the second addition. The selectivity of OH groups for isocyanate functionality is decreased by high temperatures and catalytic systems [44].

Table 2: Chemical structure of common isocyanates [43,44]**.**

Isocyanate	Chemical Structure	k_1	k_1/k_2
2,4-TDI		400	12.121
MDI		320	2.909
HDI		1	2.000
HMDI		0.57	1.425
IPDI		0.62	2.695

3.2. Polyols:

Polyols are used to prepare polyurethanes by reacting with isocyanates. Polyols are classified into two main classes: ether polyols and ester polyols. Ether polyols are characterized by their low production cost, resistance to degradation, uniform weight equivalent, and low viscosity. However, one of the disadvantages of ether polyols is their lower resistance to oxidation than polyester polyol foam. Polyester polyols are highly polarized and produce polyurethanes with high cohesive and adhesive strength, consequently, high strength and corrosion resistance. The most often used preparation agents, ethylene glycol, propylene glycol, ethylene oxide, propylene oxide, and THF, react with an epoxide (ethylene oxide) to produce ether polyols (figure 4) [2].

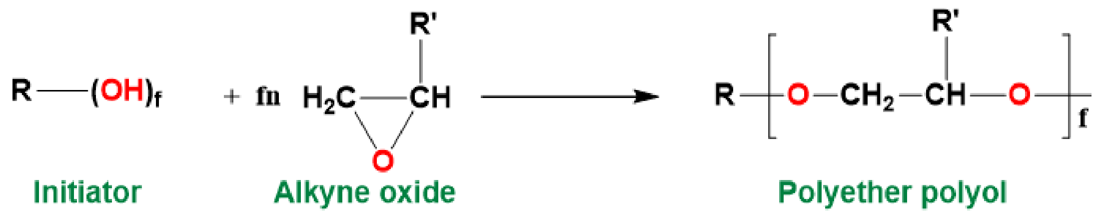
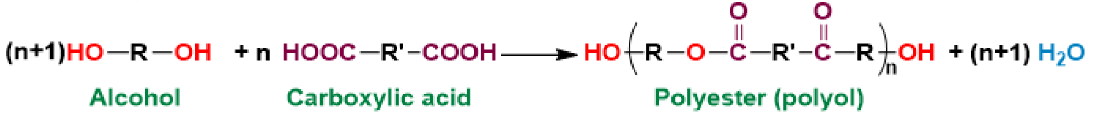


Figure 4: Example of anionic polymerization of alkylene oxides.

Polyester polyols can be made via ring-opening polymerization of lactone with a polyol (figure 6) or by the poly condensation reaction of polyols with multifunctional carboxylic acids (figure 5). Examples of substances used in the production of polyester polyols include azelaic or adipic acid as carboxylic acids and glycerol, Tri methylpropane, and diethylene glycol as polyols [2].



$$(n+1)HO-R-OH + n\,HOOC-R'-COOH \longrightarrow HO\left(R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-R\right)_n OH + (n+1)\,H_2O$$

Figure 5. An illustration of the polycondensation procedure used to produce polyester polyols.

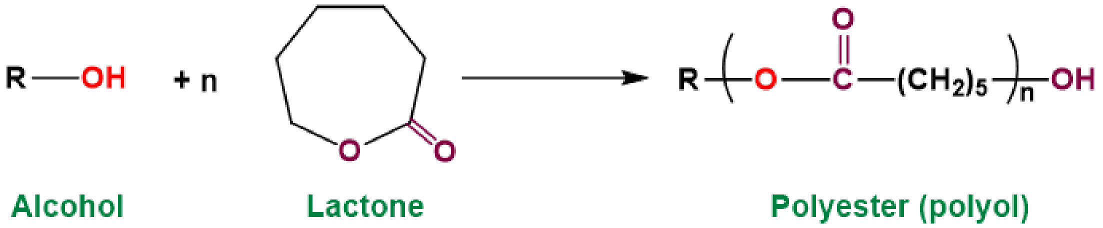


Figure 6. Example of the ring-opening polymerization of lactones to obtain polyester polyols. **n** is the number of moles of lactone molecules.

Catalyst:

Catalytic agents often incorporated into PU materials may be categorized into two primary groups: metal complex compounds and amine-based compounds. Triethylenediamine (TEDA), 1,4-diazabicyclo[2.2.2]octane (DABCO), dimethyl cyclohexylamine (DMCHA), and dimethylethanolamine (DMEA) are examples of tertiary amine compounds that are typically found in amine catalytic systems. The capacity of tertiary amine catalytic systems to ease isocyanate trimerization processes, urea synthesis, or urethane creation determines which ones are chosen. Bismuth, lead, zinc, tin, and mercury-derived metal complex compounds may also function as catalytic agents in the urethane production process. Mercury carboxylate compounds have shown exceptional efficacy in the production of PU sealant materials, coating systems, and elastomeric goods. Their higher selectivity for reactions involving polyols and isocyanates is the cause of this. However, carboxylate compounds made from zinc and bismuth have recently been used as substitute materials due to their known toxicity. Additionally, alkyl tin carboxylate, mercaptide, and oxide compounds are used in a variety of application kinds. Because tin carboxylate compounds may experience unfavorable hydrolytic effects, tin mercaptide compounds are usually added to formulations that have water. Selective use of catalytic systems is common; for example, new CuCo2O4/graphitic carbon nitride nanohybrid materials are used to lower carbon monoxide emissions and fire risks [45]. The chemical makeup of catalytic systems also affects how successful they are. For instance, aqueous polyurethane materials based on isophorone diisocyanate molecules were successfully prepared using zirconium and tin catalytic systems. While the effectiveness of zirconium catalytic systems was constant, the effectiveness of tin catalytic systems varied with various isocyanate compounds [46].

3.3. Chain extenders and cross linkers.

These compounds perform major and significant roles in polyurethane morphology: chain extension agents (f = 2) and cross-linking agents (f = 3 or higher), which typically end with amino and carboxyl functionalities and possess low molecular weight characteristics. These materials effectively improve the morphological characteristics of polyurethane adhesive systems, fiber materials, synthetic elastomers, and various other cellular and leather micro foam applications [47,48]. The copolymer interface between soft and hard segments inside the polymer structure gives these compounds their elastomeric properties. As a result, the soft segment amorphous polyester (or polyether) domains cross-link with the hard segment urethane domains. The incompatibility and immiscibility (when both phases stay amorphous) between the hard segments (high melting temperature) and the soft segments (low melting temperature and non-polar nature) cause this interfacial separation. Thus, phase separation events are not influenced by crystallization processes. Covalent bonding between hard segments (isocyanate-derived) and flexible segments (polyol-derived) prevents plastic flow within polymer chains, producing elastomeric resilience. Mechanical deformation also causes soft segment uncoiling, resulting in hard segmental alignment along the stress direction. The presence of strong hydrogen bonding produces tear resistance, high tensile strength, and excellent elongation characteristics [49-51]. The flexural, thermal, and chemical resistance of PU materials can all be affected by the choice of chain extension agents. 1,4-butanediol (BDO), cyclohexane dim ethanol, ethylene glycol, hydroquinone bis(2-hydroxyethyl) ether (HQEE), and 1,6-hexanediol are a few of the often-used chain extension agents. Figures 7 and 8 show examples of biodegradable PU materials and their synthesis processes using ethylene glycol and water as chain extension agents. Thermoplastic polyurethane (PU) products may be made using these glycol compounds. They may also be treated in the molten stage and generate well-organized hard segment domains that separate efficiently. Ethylene glycol is the only exception, since its generated bis-phenyl compound is prone to undesired breakdown as hard segment levels rise [52].

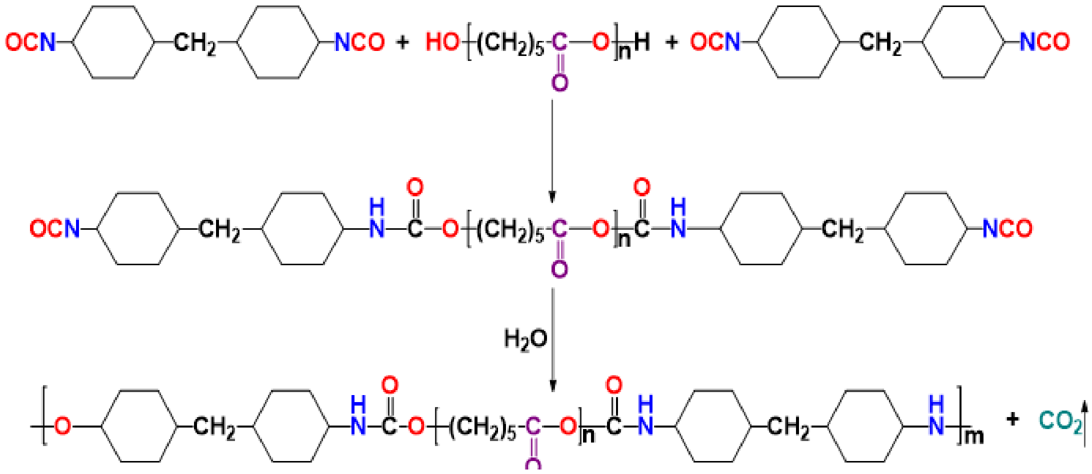


Figure 7: Example of biodegradable PUs and their synthetic routes using water as chain extenders.

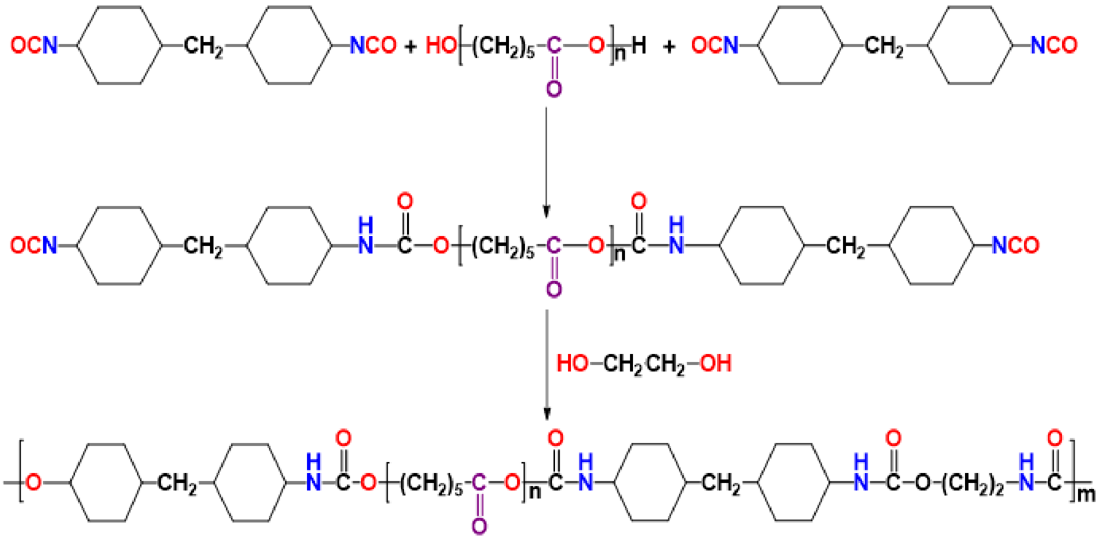


Figure 8: An illustration of biodegradable polyurethanes and their production processes that use ethylene glycol as a chain extender.

3.4. Surfactant

Surfactants (foam stabilizers) are used in the preparation of polyurethane foam. These compounds consist of copolymers [53]. The most used surfactants are polydimethylsiloxane-polyoxyalkylene copolymers (figure 9). These copolymers are linear or branched, and the hydrophilic (oxyalkylene chain) and hydrophobic (water-repellent) ends significantly influence the functionality of surfactants [2].

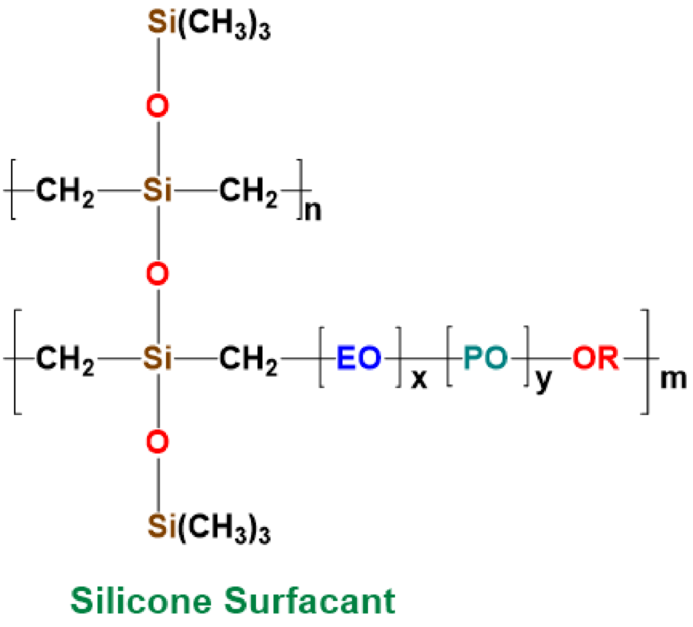


Figure 9: Chemical structure of polydimethylsiloxane-polyoxyalkylene copolymers.

Surfactants work in three ways: first, by forming bubbles that cause foam cells by lowering the surface tension of the polyurethane-air interface. Second, by preventing collapse and organizing subsurface voids by stabilizing the foam structure. Third, by increasing the concentration of available reagents by creating emulsions for the components, which influence the rate of reactions [53-56]. Although the cell structure of the end rigid and flexible foams and the compatibility of the initial ingredients vary, surfactants often behave similarly for both types of foams. Flexible foams have homogeneously miscible beginning ingredients and open cells, while stiff foams have incompatible starting materials and fully closed cells [54].

3.5. Blowing agent

Expansion in polyurethane foam occurs through a physical or chemical blowing agent, or both. The foaming methods of polyurethanes are presented graphically in **Figure 10**. The gas that causes the polyurethane foam to expand by evaporation during the foam manufacturing process is provided by the physical agent through an endothermic reaction. Low-boiling solvents like acetone, hexane, pentane, hydrofluoroolefins, or hydrofluorochlorocarbons are examples of physical blowing agents [57]. HFOs and CFCs were widely used as physical blowing agents until recently, but their destruction of the ozone layer led to their eventual restriction. Chemical blowing agents, which are substances that release gas during foam formation because of heat breakdown or chemical reactions, like water, are crucial to the manufacturing of polyurethane [58]. In industrial applications, environmentally benign substances including water, hydrofluoroolefins, and cyclopentane are often utilized. However, the CP could become clogged because of the heat produced during foaming. The CO_2 produced during exothermic processes in the manufacture of water-blown polyurethanes shows how water functions as a chemical blowing agent to expand polyurethane (Figures 11, 12, 13). The quantity of the resultant agent determines the foam density, cellular microstructure, and polymer morphology of polyurethane. As a result, the agent is involved in: Blowing agents are crucial to the manufacture of polyurethane [58]. Polyurethane foams must have closed rings or keep the blowing agent inside their cellular structure since thermal conductivity is a crucial consideration in thermal insulation applications. Therefore, using blowing agents with low thermal conductivity or ones that efficiently stay in the foam for extended periods of time is essential to enhancing the thermal characteristics of polyurethane [58]. For instance, CO_2 leaves the foam in less than a month, while HCFCs or CP stay in the foam for longer [59].

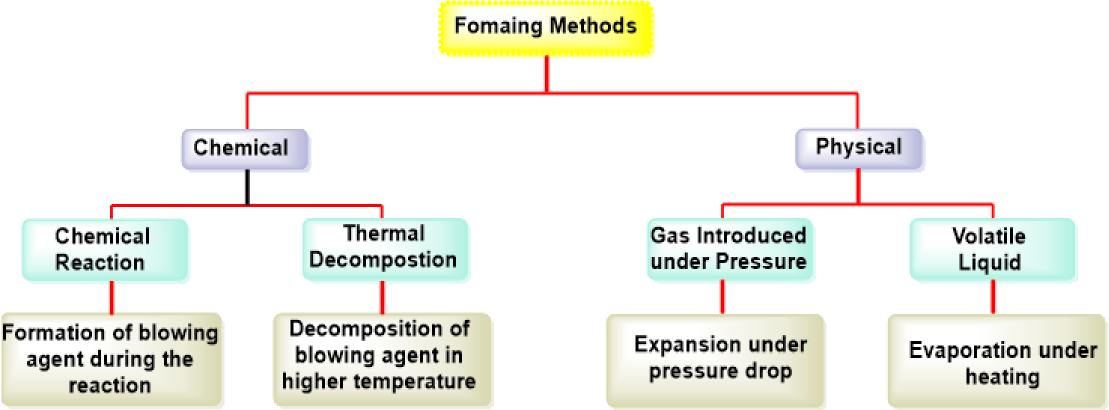


Figure 10: Division of foaming methods of polyurethanes

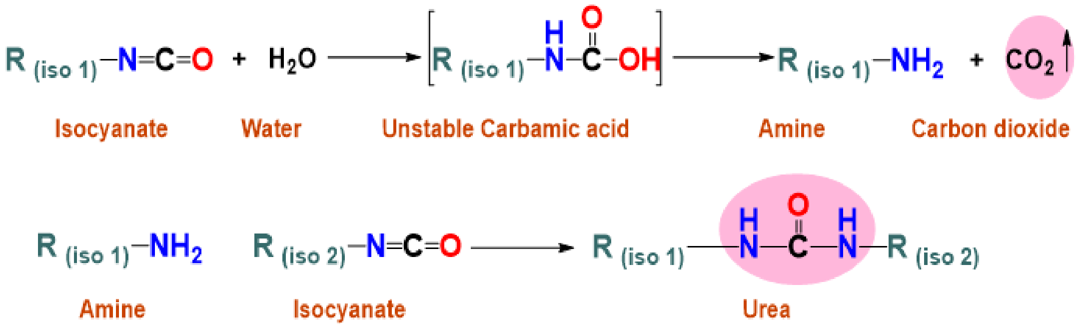


Figure 11: The process by which isocyanate and water combine to produce urea and carbon dioxide is known as the "foaming" or "blowing" reaction. The structures of the polyol and isocyanate are denoted by polyol and Riso, respectively.

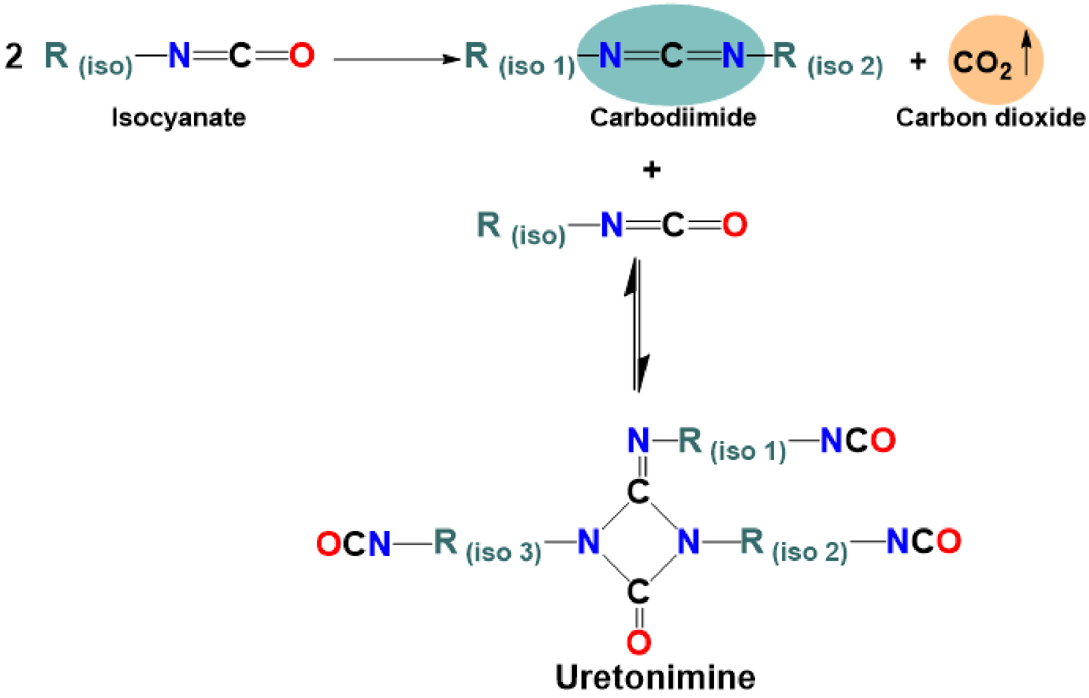


Figure 12: Isocyanate dimerizes to create carbon dioxide and carbodiimide, which then react to form uretonimine using carbodiimide. The structure of isocyanate is called Riso.

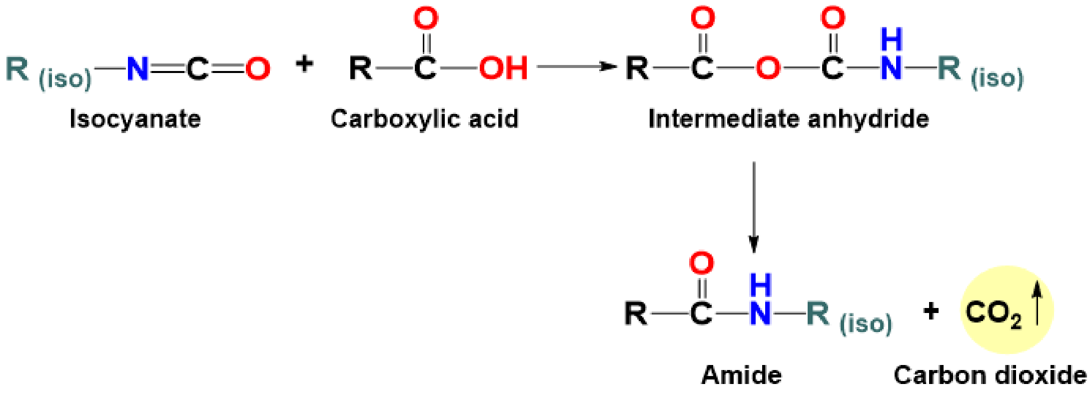


Figure 13: The process by which isocyanate and carboxylic acid combine to produce the final amide and the intermediate anhydride. Riso is the isocyanate's structure.

4. Application of polyurethanes:

The physical and chemical properties of polyurethane depend on the polyol and isocyanate used. The type of polyurethane used figures out between 60% and 70% of its properties. Polymer properties can be significantly modified by varying the chain length, molecular structure, and function of the polyol chain using elements such as fluorine, acrylic, and rubber. This customization has given polyurethanes an advantage in many industrial applications, including coatings, adhesives, sealants, and elastomers (CASE) [60-63], automotive [64,65], medical [66-75], textiles and apparels [76-81], marine [82-91], and Polyurethane wood composites [92-97].

Conclusions:

From this review, it is concluded that the diverse structural composition of polyurethane gives it great flexibility in design and wide-ranging application. Furthermore, its preparation agents, polyisocyanates and polyols, and the possibility of introducing variable additives such as chain extenders, blowing agents, and catalysts, provide a wide scope for modification and customization to suit the various requirements of the era. The unique physical and chemical properties of polyurethane, such as chemical, mechanical, and thermal resistance, flexibility, and stiffness, have enabled its rapid spread in various applications, such as plastics, coatings, adhesives, the automotive industry, and textiles. This confirms its importance as a material capable of outperforming and adapting many other polymers in industrial uses.

References:

[1] Wang, H., Li, T., Li, J., Zhao, R., Ding, A., & Xu, F. J. (2024). Structural engineering of polyurethanes for biomedical applications. Progress in Polymer Science, 151, 101803. https://doi.org/10.1016/j.progpolymsci.2024.101803

[2] Ashida, K. (2006). Polyurethane and related foams: chemistry and technology. CRC press.

[3] Szycher, M. (Ed.). (1999). Szycher's handbook of polyurethanes. CRC press.

[4] Prisacariu, C. (2011). Polyurethane elastomers: from morphology to mechanical aspects. Springer Science & Business Media.

[5] Król, P. (2008). Linear polyurethanes: synthesis methods, chemical structures, properties, and applications. CRC Press.

[6] Brains, P. F. (1969). Polyurethanes technology. Hoboken: John Wiley & Sons.

[7] Hepburn, C. (2012). Polyurethane elastomers. Springer Science & Business Media.

[8] Wirpsza, Z. (1993). Polyurethanes: chemistry, technology, and applications. Ellis Horwood.

[9] J. Dodge, Polyurethane Chemistry, Second ed., Bayer Corp., Pittsburgh, PA, 1999.

[10] Bayer, A. G. (1979). Polyurethane Application Research Department,‘‘Bayer-Polyurethanes,” Leverkusen, Germany. Edition January.

[11] Hernandez-Hernandez, M. E. (1994). Thermal stability of polyurethanes: Applications to polymer processing and recycling. University of Minnesota.

[12] Darby, R. T., & Kaplan, A. M. (1968). Fungal susceptibility of polyurethanes. Applied microbiology, 16(6), 900-905.

[13] Martens, R., & Domsch, K. H. (1981). Microbial degradation of polyurethane foams and isocyanate based polyureas in different media. Water, Air, and Soil Pollution, 15(4), 503-509.

[14] Crabbe, J. R., Campbell, J. R., Thompson, L., Walz, S. L., & Schultz, W. W. (1994). Biodegradation of a colloidal ester-based polyurethane by soil fungi. International Biodeterioration & Biodegradation, 33(2), 103-113.

[15] Nakajima-Kambe, T., Onuma, F., Kimpara, N., & Nakahara, T. (1995). Isolation and characterization of a bacterium which utilizes polyester polyurethane as a sole carbon and nitrogen source. FEMS microbiology letters, 129(1), 39-42.

[16] Akutsu, Y., Nakajima-Kambe, T., Nomura, N., & Nakahara, T. (1998). Purification and properties of a polyester polyurethane-degrading enzyme from Comamonas acidovorans TB-35. Applied and environmental microbiology, 64(1), 62-67.

[17] Howard, G. T., Ruiz, C., & Hilliard, N. P. (1999). Growth of Pseudomonas chlororaphis on apolyester–polyurethane and the purification andcharacterization of a polyurethanase–esterase enzyme. International biodeterioration & biodegradation, 43(1-2), 7-12.

[18] Nakajima-Kambe, T., Shigeno-Akutsu, Y., Nomura, N., Onuma, F., & Nakahara, T. (1999). Microbial degradation of polyurethane, polyester polyurethanes, and polyether polyurethanes. Applied microbiology and biotechnology, 51(2), 134-140.

[19] Howard, G. T. (2002). Biodegradation of polyurethane: a review. International Biodeterioration & Biodegradation, 49(4), 245-252.

[20] Izarra, I.; Borreguero, A.M.; Garrido, I.; Rodríguez, J.F.; Carmona, M. Comparison of flexible polyurethane foams properties from different polymer polyether polyols. Polym. Test. **2021**, 100, 107268. [CrossRef]

[21] Yick, K.-l., et al., “Study of thermal–mechanical properties of polyurethane foam and the three-dimensional shape of molded bra cups,” Journal of Materials Processing Technology, 210(1): p. 116-121, 2010.

[22] TeodorSocaciu, Mihai Simon, LiviuDorin Pop, ManuelFreitas, “Research and application of visco-elastic memory foam in the field of footwear manufacturing.” Scientific Bulletin of the PetruMaior University of TirguMures, Vol. 7, No.2, 2010.

[23] Richard S. Schmidt: “NASA pressure relieving foam technology is keeping the leading inner-spring mattress firms awake at night.” Technovation 29 181-191, 2009.

[24] Krupers, M.J., et al., “Formation of rigid polyurethane foams with semi-fluorinated diblock copolymeric Surfactants,” Polymer, 39(10): p. 2049-2053, 1998.

[25] Ligoure, C., et al., “Making polyurethane foams from microemulsions.” Polymer, 46(17): p. 6402-6410, 2005.

[26] Malak, S.F.F. and I.A. Anderson, “Orthogonal cutting of polyurethane foam,” International Journal of Mechanical Sciences, 47(6): p. 867-883, 2005.

[27] Marsavina, L. and T. Sadowski, “Dynamic fracture toughness of polyurethane foam,” Polymer Testing, 27(8): p. 941-944, 2008.

[28] Singh, R., P. Davies, and A.K. Bajaj, “Identification of Nonlinear and Viscoelastic Properties of Flexible Polyurethane Foam,” Nonlinear Dynamics, 34(3-4): p. 319-346, 2003.

[29] Urgun-Demirtas, M., D. Singh, and K. Pagilla, “Laboratory investigation of biodegradability of a polyurethane foam under anaerobic conditions,” Polymer Degradation and Stability, 92(8): p. 1599-1610, 2007.

[30] Shoaib Suleman, S. M. K., Tahir Jamil, Waqas Aleem, Muhammad Shafiq and Nafisa Gull, “Synthesis and Characterization of Flexible and Rigid Polyurethane Foam” , Asian Journal of Applied Sciences, 2(5): p. 701-710, 2014.

[31] Ulrich, H. (1996). Chemistry and technology of isocyanates. *(No Title)*.

[32] Islam MR, Beg MDH, Jamari SS. Development of vegetable-oil-based polymers. J. Appl. Polym. Sci. 2014;131(18):40787-90. DOI: 10.1002/app.40787

[33] Ionescu M. Chemistry and technology of polyols for polyurethanes, Rapra Technology, Shrewsbury, UK, Polymer International, 56, 2007

[34] Bayer, O. (1947). Polyurethanes. Mod Plast, 24, 149-152.

[35] Christian Six; Frank Richter (2005). "Isocyanates, Organic". Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH. doi:10.1002/14356007.a14_611. ISBN 978-3-527-30673-2.

[36] Arnold, S. R., Nelson, J. A., & Verbanc, J. J. (1957). Recent advances in isocyanate chemistry. Chemical reviews, 57(1), 47-76.

[37] Peyrton, J., & Averous, L. (2021). Structure-properties relationships of cellular materials from biobased polyurethane foams. Materials Science and Engineering: R: Reports, 145, 100608.

[38] J. H. Saunders and R. J. Slocombe, Chem. Rev., 1948, 43,203-218.

[39] S. Ozaki, Chem. Rev., 1972, 72, 457–496.

[40] Delebecq, E., Pascault, J. P., Boutevin, B., & Ganachaud, F. (2013). On the versatility of urethane/urea bonds: reversibility, blocked isocyanate, and non-isocyanate polyurethane. Chemical reviews, 113(1), 80-118.
[41] Allport, D. C., Gilbert, D. S., & Outterside, S. M. (Eds.). (2003). MDI and TDI: safety, health, and the environment: a source book and practical guide. John Wiley & Sons.
[42] Chattopadhyay, D. K., & Raju, K. V. S. N. (2007). Structural engineering of polyurethane coatings for high performance applications. Progress in polymer science, 32(3), 352-418.
[43] M. Ionescu, Chemistry and technology of polyols for polyurethanes, Rapra Technology, Shawbury, Shrewsbury, Shropshire, UK, 2005.
[44] Szycher, M. (Ed.). (1999). Szycher's handbook of polyurethanes. CRC press.
[45] Shi, Y., Yu, B., Zhou, K., Yuen, R. K., Gui, Z., Hu, Y., & Jiang, S. (2015). Novel CuCo2O4/graphitic carbon nitride nanohybrids: Highly effective catalysts for reducing CO generation and fire hazards of thermoplastic polyurethane nanocomposites. Journal of hazardous materials, 293, 87-96.
[46] Sardon H, Irusta L, Fernández-Berridi MJ. Synthesis of isophorone diisocyanate (IPDI) based waterborne polyurethanes: Comparison between zirconium and tin catalysts in the polymerization process. Prog. Organ. Coatings 2009;66:291–295.
[47] Kirchmeyer S, Müller H-P, Ullrich M, Liesenfelder U. Homogeneously mixing polyisocyanate, zerewitinofff active hydrogen compound, and chain extender for condensation polymerization; continuous degassing and extrusion, ed: Google Patents, 2002.
[48] Yamasaki S, Nishiguchi D, Kojio K, Furukawa M. Effects of polymerization method on structure and properties of thermoplastic polyurethanes. J. Polym. Sci. Part B: Polym. Phy. 2007;45:800-814.
[49] Blackwell J, Gardner KH. Structure of the hard segments in polyurethane elastomers. Polym. 1979;20:13-17.
[50] Grillo D, Housel T. Physical properties of polyurethanes from polyesters and other polyols. J. Soc. Plast. Ind. Inc. 1992;52-67.
[51] Musselman S, Santosusso T, Sperling L. Structure versus performance properties of cast elastomers, in Polyurethanes' 98 Conference Proceedings, 1998.
[52] E. D. Weil, Reaction polymers, Wilson F. Gum, Henri Ulrich, and Wolfram Riese, eds., Hanser Publishers, Munich, Germany, 1992, 838, Oxford University Press, New York, ed: Wiley Online Library, 1993.
[53] M.F. Sonnenschein, Polyurethanes: Science, Technology, Markets, and Trends, 2015.
[54] M. Szycher, Szycher's Handbook of Polyurethanes, Second ed., CRC Press Boca Raton, Florida, USA, 2012.
[55] Akindoyo, J. O., Beg, M. H., Ghazali, S., Islam, M. R., Jeyaratnam, N., & Yuvaraj, A. R. (2016). Polyurethane types, synthesis, and applications–a review. Rsc Advances, 6(115), 114453-114482.
[56] Yang, C.G., L. Xu, and N. Chen, “Thermal expansion of polyurethane foam at low temperature,” Energy Conversion and Management, 48(2): p. 481-485, 2007.
[57] K.H. Choe, D.S. Lee, W.J. Seo, W.N. Kim, Properties of Rigid Polyurethane Foams with Blowing Agents and Catalysts, Polymer Journal, 36 (2004) 368-373.
[58] Handbook of Polymer Foams, Rapra Technology Limited, Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK, 2004.
[59] S. Estravís, J. Tirado-Mediavilla, M. Santiago-Calvo, J.L. Ruiz-Herrero, F. Villafañe, M.A. Rodríguez-Pérez, Rigid polyurethane foams with infused nanoclays: Relationship between cellular structure and thermal conductivity, European Polymer Journal, 80 (2016) 1–15.
[60] Petrović, Z. S., Wan, X., Bilić, O., Zlatanić, A., Hong, J., Javni, I., ... & Degruson, D. (2013). Polyols and polyurethanes from crude algal oil. Journal of the American Oil Chemists' Society, 90(7), 1073-1078.

[61] Y. Xu, Z. Petrovic, S. Das, G.L. Wilkes, Morphology, and properties of thermoplastic polyurethanes with dangling chains in ricinoleate-based soft segments, Polymer 49 (2008) 4248e4258.

[62] S. Dutta, N. Karak, Synthesis, Characterization of Poly (Urethane Amide(Resins From Nahar Seed Oil For Surface Coating Applications 53, 2005, pp. 147e152.

[63] S. Dutta, N. Karak, T. Jana, Progress in Organic Coatings Evaluation of Mesua ferrea L. Seed Oil Modified Polyurethane Paints 65, 2009, pp. 131e135.

[64] J. Njuguna, K. Pielichowski, K. Kayvantash, A.C. Walton, Fabrication , Characterization and Low-Velocity Impact Testing of Hybrid Sandwich Composites with Polyurethane/Layered Silicate Foam Cores, 2011, https://doi.org/10.1002/pc.

[65] R. Deng, P. Davies, A.K. Bajaj, Flexible Polyurethane Foam Modelling And Identification of Viscoelastic Parameters for Automotive Seating Applications 262, 2003, pp. 391e417.

[66] A. Domanska, A. Boczkowska, Biodegradable polyurethanes from crystalline prepolymers, Polym. Degrad. Stabil. 108 (2014) 175e181.

[67] B. Zhou, Y. Hu, J. Li, B. Li, Chitosan/phosvitin antibacterial films fabricated via layer-by-layer deposition, Int. J. Biol. Macromol. (2013) 1e7, https://doi.org/10.1016/j.ijbiomac.2013.12.016.

[68] X. Zhou, T. Zhang, D. Guo, N. Gu, Colloids and Surfaces A: physicochemical and Engineering Aspects A facile preparation of poly (ethylene oxide(-modified medical polyurethane to improve hemocompatibility, Colloids Surfaces A Physicochem. Eng. Asp. 441 (2014) 34e42.

[69] D.H. Owen, D.F. Katz, A Vaginal Fluid Simulant. 7824, 1999, 0e4.

[70] L. Be, et al., Vivo Semen-Associated pH Neutralization of Cervicovaginal Secretions ,1997 ,4pp. 367e374.

[71] A. Solanki, S. Thakore, Ac ce p te d us cr t, Int. J. Biol. Macromol. (2015,(https://doi.org/10.1016/j.ijbiomac.2015.07.003.

[72] M. Naeem, W. Kim, J. Cao, Y. Jung, J. Yoo, Enzyme/pH dual sensitive polymeric nanoparticles for targeted drug delivery to the inflamed colon, Colloids Surf. B Biointerfaces (2014), https://doi.org/10.1016/j.colsurfb.2014.09.026.

[73] T. Yamaoka, Y. Makita, H. Sasatani, S. Kim, Linear Type Azo-Containing Polyurethane As Drug-Coating Material For Colon-Specific Delivery: Its Properties, Degradation Behavior, And Utilization For Drug Formulation 66, ,2000pp. 187e197.

[74] M.R. Clark, et al., A Hot-Melt Extruded Intravaginal Ring For The Sustained Delivery Of The Antiretroviral Microbicide UC781 101, 2012, pp. 576e587.

[75] A. Solanki, J. Mehta, S. Thakore, Structure e property relationships and biocompatibility of carbohydrate crosslinked polyurethanes, Carbohydr. Polym. 110 (2014) 338e344.

[76] S. Xinrong, W. Nanfang, S. Kunyang, D. Sha, C. Zhen, Journal of Industrial andEngineering Chemistry Synthesis and characterization of waterborne polyurethane containing UV absorption group for finishing of cotton fabrics, J. Ind. Eng. Chem. (2013), https://doi.org/10.1016/j.jiec.2013.12.003.

[77] Y. Yikai, Z. Yuejun, Review of study on resin dye-fixatives on cotton fabrics, Mod. Appl. Sci. 3 (Sep. 2009).

[78] H. Wang, C. Gen, Synthesis of Anionic Water-Borne Polyurethane with the Covalent Bond of a Reactive Dye, 2002, pp. 797e805, https://doi.org/10.1002/app.10336.

[79] S. Muzaffar, I. Ahmad, M. Zuber, H. Nawaz, M. Shahid, International Journal of Biological Macromolecules Synthesis , characterization and efficiencyevaluation of chitosan-polyurethane based textile finishes, Int. J. Biol. Macromol. 145 (2016) 93e155.

[80] G. Mazzon, et al., Applied Surface Science Hydrophobic treatment of woven cotton fabrics with polyurethane modi fi ed aminosilicone emulsions, Appl. Surf. Sci. 490 (2019) 331e342.

[81] M. Sultan, et al., Progress in Organic Coatings Impact of soft segment size on physicochemical and antimicrobial

properties of waterborne polyurethane dispersions for textile applications, Prog. Org. Coating 133 (2019) 174e179.

[82] Y.P. Chin, S. Mohamad, M. Radzi, B. Abas, Removal of Parabens from Aqueous Solution Using b -Cyclodextrin Cross-Linked Polymer, 2010, pp. 3459-3471, https://doi.org/10.3390/ijms11092459.

[83] J.O. Akindoyo, M.D.H. Beg, S. Ghazali, M.R. Islam, RSC Advances. RSC Adv. 6 (2016) 114453-114482.

[84] P. Chem, P. Xiao, Y. Dudal, P.F. Corvini, P. Shahgaldian, Polymer Chemistry Cyclodextrin-Based Polyurethanes Act as Selective Molecular Recognition Materials of Active Pharmaceutical Ingredients (APIs), 2011, pp. 1264e1266, https://doi.org/10.1039/c1py00114k.

[85] S. Nasiri, N. Alizadeh, Synthesis and adsorption behavior of hydroxypropylb-cyclodextrinepolyurethane magnetic nanoconjugates for crystal and methyl violet dyes removal from aqueous solutions, RSC Adv. 9 (2019) 24603-24616.

[86] A. Biswas, M. Appell, Z. Liu, H.N. Cheng, Microwave-assisted synthesis of cyclodextrin polyurethanes, Carbohydr. Polym. 133 (2015) 74-79.

[87] E.A. Moawed, A.B. Abulkibash, M.F. El-shahat, Synthesis and characterization of iodo polyurethane foam and its application in removing of aniline blue and crystal violet from laundry wastewater, Integr. Med. Res. (2014), https:// doi.org/10.1016/j.jtusci.2014.07.003.

[88] P. Davies, G. Evrard, Accelerated Ageing of Polyurethanes for Marine Applications, vol. 92, 2007, pp. 1455-1464.

[89] S.A. Yesudass, S. Mohanty, S.K. Nayak, C.C. Rath, Zwitterionic e polyurethane coatings for non-specific marine bacterial inhibition: a nontoxic approach for marine application, Eur. Polym. J. 96 (2017) 304-315.

[90] L. Mishnaevsky, J. Sütterlin, Micromechanical model of surface erosion of polyurethane coatings on wind turbine blades, Polym. Degrad. Stabil. 166 (2019) 283-289.

[91] V.A. Mooss, F. Hamza, S.S. Zinjarde, A.A. Athawale, Polyurethane films modified with polyaniline-zinc oxide nanocomposites for biofouling mitigation, Chem. Eng. J. (2018) 1-11, https://doi.org/10.1016/j.cej.2018.11.038.

[92] X. Lu, J. Huang, W. Wong, J. Qu, Solar Energy Materials and Solar Cells A novel bio-based polyurethane/wood powder composite as shape-stable phase change material with high relative enthalpy e ffi ciency for solar thermal energy storage, Sol. Energy Mater. Sol. Cells 200 (2019) 109987.

[93] A. Shaaban, S. Se, I.M. Ibrahim, Q. Ahsan, Preparation of rubber wood sawdust-based activated carbon and its use as a filler of polyurethane matrix composites for microwave absorption, N. Carbon Mater. 30 (2015) 167e175.

[94] M. Fornasieri, et al., Composites: Part A Synthesis and characterization of polyurethane composites of wood waste and polyols from chemically recycled pet, Compos. Part A 42 (2011) 189e195.

[95] M.R. Patel, J.V. Patel, V.K. Sinha, Polymeric Precursors from PET Waste and Their Application in Polyurethane Coatings, vol. 90, 2005.

[96] X. Kong, L. Zhao, J.M. Curtis, Polyurethane nanocomposites incorporating biobased polyols and reinforced with a low fraction of cellulose nanocrystals, Carbohydr. Polym. (2016), https://doi.org/10.1016/j.carbpol.2016.07.032.

[97] W. Zhang, et al., Industrial Crops & Products High bio-content castor oil based waterborne polyurethane/sodium lignosulfonate composites for environmental friendly UV absorption application, Ind. Crop. Prod. 142 (2019) 111836.