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Polyurethane and its Application in Textile Industry

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Abstract: Because of obvious human requirements, the textile industry has expanded to become the second-largest manufacturing sector, immediately behind the agricultural sector. The textile industry is one of the most important and major sectors for using polymers. Polymers are important chemical components for the production of textiles. Polymers are used at every step of the textile production process, from developing fiber to coloring and finishing textiles. Polyurethanes (PUs) are a multilateral polymer category with various structures, shapes, and behavior under varied conditions that are thought to be beneficial for many useful and intelligent reactions. For a variety of applications, PU has recently increasingly gained scientific attention. The most recent advancements in PU for textile applications are covered in this review article.

Keywords: polymers; textile industry; polyurethane.

1. Introduction

Physical and inorganic chemists frequently use the term “polymer” to refer to ill-defined molecular aggregates, although organic scientists generally agree that polymerization is a chemical combination involving the operation of primary valence forces [1]. However, there is not much acceptance beyond this. When two compounds may have the same content but different molecular weights, Berzelius created the term “polymer” to describe them. He categorized polymerize as a particular type of isomerism [2].

The commonly accepted definition of these terms has since undergone significant change, but the definitions found in modern textbooks consistently state that a monomer and its polymer share the same chemical components and that polymerization is unique to unsaturated compounds and involves self-addition. However, new research shows that many cases where the phrases “polymer” and “polymerization” are used do not meet these requirements [3]. For instance, the formula for -polyoxymethylene is $(CH_2O)\ xH_2O$ rather than $(CH_2O)x$. It is also true that many non-unsaturated molecules can interact with one another to produce high-molecular-weight byproducts, a process known as polymerization [4]. For instance, benzyl chloride in the existence of aluminum chloride:

$$x\ C_6H_6CH_2CI \longrightarrow (C_7H_6)x + x\ HCI$$

The elimination of HCl to produce the radical $CsH_6CH=$, which is unsaturated and capable of interacting with itself via addition, is likely the first step in this reaction [5]. On the

other hand, possible that this is a polymolecular Friedel Crafts reaction, with the creation of $C_6H_5CH_2$-$C_6H_5CH_2C1$ as the first step. This compound can then interact with itself through the same process to produce a very long chain with little to no chlorine. If the conventional definitions are used, only if the reaction follows the first mechanism can it be appropriately referred to as polymerization [6].

Surprisingly, there are instances in the literature where a reaction named polymerization is used to demonstrate that the initial step must involve the production of an unsaturated intermediate capable of reacting with itself by addition. Perhaps it is unnecessary to mention that the concerns related to the creation of high polymers and the mechanism by which they form are frequently rather complex and, by definition, cannot be answered beforehand [7].

It is more useful and practical to define polymerization as any chemical fusion of several related molecules into a single molecule (which is also more consistent with real usage). Then, a chemical will be considered a polymer if it can be created through this process or destroyed through the opposite process [8]. For example, formaldehyde can be created from polyoxymethylene by the action of heat, ethylene glycol can be created from polyethylene glycol by hydrolysis, cellulose can be converted to glucose through hydrolysis, and rubber can be created when isoprene reacts with itself [9].

2. Polymer Structure

The structure of the individual repeating units in atomic detail governs the shape of molecular chains, affecting plastic products' general characteristics. The type of repeating units, functional groups, branches, potential cross-links, and the type of monomer producing the chain are all factors in these microstructure configurations. The order in which the repeating units are arranged and the way they interact with one another directly affect the cohesive forces, packing density, strength, flexibility, elongation, and molecular mobility of the polymer, which in turn regulates the overall behavior of the plastic and its use. The following sections explain various polymer structures caused by certain configurations and interactions between the repeating units and polymer chains [10,11].

2.1. Linear, branched, and cross-linked polymers.

Depending on the intermolecular links between the constituent chains, polymeric materials can be linear, branched, or cross-linked. The chain structures of linear, branched, and cross-linked polymers are shown in Fig. 1.

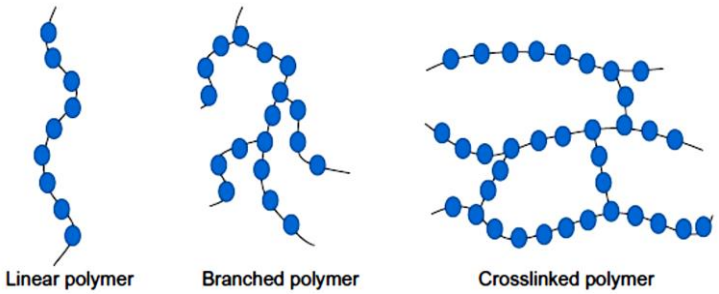


Figure 1. Schematic representation of linear, branched, and cross-linked polymers.

Because their molecules are long chains constructed from a repeating radical or unit, the simplest, most common, and possibly most significant high polymers can be identified

structurally. This kind of structure may be described by the general formula, -A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-.

The structural unit is the repeating radical -A-. The quantity and type of these units determine the molecule's composition. The position of the terminal valences must be specified to complete this formula; they might theoretically be saturated by univalent groups or connected to form a cyclic structure. Polymers in this class are referred to as linear polymers, regardless of whether the chain is open or closed. It should be noted that high linear polymers typically consist of mixes of chains with various lengths [12,13].

The structural units of the chain will generally be identical if the polymer is produced from a single compound; however, chains made up of two or more different structural units may result from the mutual reaction of two or more chemically similar but not identical compounds. Linear mixed polymers will be the name given to such items. This class includes a large number of proteins and polypeptides. There are also non-linear polymers, which can be created, for instance, by cross-linking lengthy chains into two- or three-dimensional structures [14,15].

2.1.1. Linear polymers.

The repeating units are connected end to end to form a single flexible chain in linear polymers. The physical attractions hold the polymeric chains together. The chains are kept together by the strong van der Waals attractions of these polymers. Typically, monomers with a single end group are used to create linear polymers. Branched polymers are not considered to be linear polymers that have side groups as a component of their monomer structure. Polyethylene, PVC, polystyrene, and polyamides are typical examples of linear polymers. In general, linear polymers are stiff [16,17].

2.1.2. Branched polymers.

As seen in Fig. 1, branched polymers feature side chains or branches extending from the main chain. The identical repeating units that make up the main polymer chains also make up the side chains or branches. During polymerization, side reactions leading to the branches. Branching is likely to be supported by monomers with two or more end groups [18,19].

A polymer must include at least one full monomer unit in each side chain or branch for it to be considered a branched polymer. Low-density polyethylene (LDPE), one of the most typical types, is used for various things, including coatings for packaging materials and plastic bags, containers, textiles, and electrical insulation. Due to the branched chains' decreased packing efficiency, branched polymers exhibit lower density. The difference between long- and short-branched polymers is determined by the length of the side chains or branches. Long branches may feature irregular, star-shaped, or comb-like formations. However, despite the possibility of further branching, the branches do not join with another polymer chain [20,21].

2.1.3. Cross-linked polymers.

As the name suggests, the adjacent polymer chains are linked in a three-dimensional network structure in cross-linked polymers. The linkages are also referred to as cross-links. The covalent connection between the chains or branches may have led to the cross-links. The resulting structure is depicted in Fig. 1.

Cross-links typically have a permanent character. The polymer becomes thermoset after the cross-links between the chains form. Such polymers can be identified by their cross-linking degree, which measures the number of junction points per unit volume. Typical examples include epoxies, bulk molding compounds, rubber, and different adhesives [22,23].

2.1.3.1. Types of compounds capable of polymerizing.

Fischer's well-known synthesis of polypeptides serves as an example of the sequential synthesis of lengthy molecular chains that contain repeating units. However, polymerization reactions result in the creation of polymeric chains in a single step. Simple molecules of three main sorts have this kind of self-combination ability: (α) unsaturated compounds; (b) cyclic compounds; (c) polyfunctional compounds. Illustrated by the following examples.

$$n CH_2{=}O + H_2O \longrightarrow HO\text{-}CH_2O\text{-}CH_2O\text{-}\ldots\text{-}\ CH_2O\text{-}CH_2O\text{-}H$$

Formaldehyde — α-Polyoxymethylene

$$n\ [CH_2CH_2O] + H_2O \longrightarrow HO\text{-}CH_2CH_2O\text{-}CH_2CH_2O\text{-}\ .\ .\ .\ \text{-}CH_2CH_2O\text{-}H$$

Ethylene oxide — Polyethylene glycol

$$nHO\text{-}CH_2\,CH_2O\text{-}H\text{-}(n\text{-}1)\ H2O \longrightarrow HO\text{-}\ CH_2CH_2O\text{-}\ CH_2CH_2O\text{--}\ CH_2CH_2O\text{-}H$$

Ethylene glycol — Polyethylene glycol

The product molecule in each of these cases comprises a succession of repeating, identical units. Each unit equals one molecule of the starting substance. Therefore, the latter is called the monomer (mer = component). Although they have different structures and chemical makeups, ethylene oxide and ethylene glycol are monomers since each molecule contains one $-CH_2CH_2O$ unit. Diethylene glycol, also known as $HO\text{-}CH_2CH_2O\text{-}\ CH_2CH_2O\text{-}H$, is a dimer [24,25].

2.1.3.2. Polymerization mechanisms.

Functionality refers to a repeating unit's capacity to create covalent connections with nearby molecules. The ability of the repeating units to interact with the surrounding molecules through certain reaction mechanisms might be influenced by their numerous functions. Each repeating unit with two or more functionalities has the potential to interact with nearby molecules to produce a wide range of chemical reactions. This generates a sizably huge number of potentially confusing reactions. Different polymerization processes are grouped into several groups for clarity purposes depending on their reaction mechanisms, such as addition, condensation, ring opening, and other mechanisms [26,27].

2.1.3.2.1. Addition or chain polymerization.

Addition polymerization is one of the most widespread processes. Additionally, only reactions between monomers and reactive sites on the polymer chain are used to generate the polymer chain during polymerization [28]. The chain reaction creates additional monomer units one at a time. After each growth stage, the insertion of a repeating unit into the expanding chain regenerates the reactive site, and this process is continued throughout the polymerization. A simplified version of the procedure may be described as adding each link to a bicycle chain one at a time to either or both of the chains' ends. The chain gets longer as more links are added. In addition to polymerization, unsaturated monomers (monomers with double or triple

bonds) are typically utilized. All monomers are used up during the addition polymerization, and no byproducts are produced. Polyethylene, polyvinyl chloride (PVC), acrylics, polystyrene, polytetrafluoroethylene, and polyoxymethylene are typical examples of addition polymerization (acetal) [29].

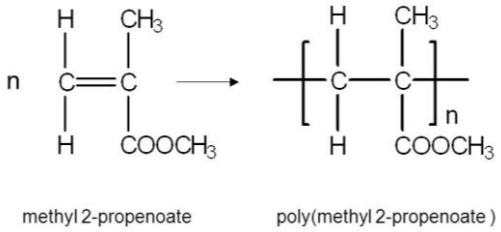


Figure 2. Addition polymerization.

Fig. 2 shows a schematic representation of addition polymerization. One can see that the repeating units on the left of the arrow are added to produce the polymer to the right of the arrow symbol. R1 and R2 in this picture stand in for functional groups or other atom groups. Functional groups are particular atomic groups that control the properties and chemical reactivity of the polymer, affecting the manufacture and use of plastic products [30].

Use the illustration of a chain for a bicycle, a necklace, or even a charm bracelet, where each link is adorned with a pendant or charm. The construction of these pendants may vary, and they may be linked to the chain in different ways, giving them distinctive qualities and appearances. Similar to this, functional groups are joined to the polymer's backbone, giving the material's use in plastics and polymers special characteristics [31]. Additionally, the polymerization reaction takes place in three separate phases, which are as follows: 1. Chain initiation: In this step, a reactive site is usually created by an external initiator, which starts the polymerization reaction. An organometallic complex, a radical (free radical polymerization), a cation (cationic polymerization, applicable to monomers with electron-donating groups like isobutylene), an anion (anionic polymerization, applicable to monomers with electron-withdrawing groups like styrene, acrylonitrile, butadiene, acrylates, ethylene oxide, and lactones), or an anion could all serve as the initiator (coordination polymerization with Ziegler-Natta catalysts). 2. Chain propagation: In this stage, repeating units or monomers attach to the molecular chain to extend its length. 3. Chain termination: In this stage, the reactive center is neutralized to stop the chain's growth [32-34].

2.1.3.2.2. Condensation polymerizations or step-growth polymerization.

The second most frequent method for polymerization is condensation polymerization (as the waste condenses out). In this mechanism, a tiny molecule (condensate) like water or hydrochloric acid is released due to the reaction between the repeating units and the expanding chain. Step-growth polymerization is so named because the reaction proceeds in steps [35].

Polyesters, polyamides, polycarbonates, proteins, and polysaccharides are typical examples. It should be noted that plastics produced via condensation polymerization, in which water is liberated, such as polyesters and polyamides, are prone to deterioration when exposed to water at high temperatures. Thus, for these polymers to melt properly, low moisture levels and dry conditions are required. Any two types of molecules, including monomers, dimers, trimmers, and oligomers, can interact with one another during condensation polymerization to form a larger molecule [36].

As shown in Fig. 3, step-growth polymerization typically (though not always) mixes two distinct components in an alternating structure. Each monomer has two functionalities since it has at least two reactive sites. If the tiny molecule byproduct is not removed, the step-growth reversible process achieves equilibrium and ends [37].

Polar functional groups are frequently present on the chains, which strengthens the attraction between the chains and boosts crystallinity and tensile strength. Condensation polymerization uses monomers distinct from addition polymerization in that they have functional groups, and each monomer has at least two reactive sites (usually representative of two different functional groups) [38].

Condensation polymerization typically grows stepwise by carbon-heteroatom bond formation, such as C-O or C-N, in contrast to addition polymerization, which grows quickly from the formation of C-C bonds. The molecular weight of the polymer rises steadily throughout the reaction and requires a long reaction time to reach a higher molecular weight. In the last phases of polymerization, groups of shorter chains merge into larger chains because the terminal functional groups on a chain remain active [39].

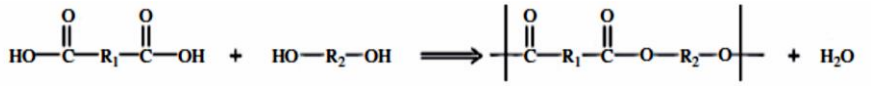


Figure 3. Condensation polymerization with the elimination of water.

A general class of condensation polymerizations is represented by the equation

$$\text{-X-R-y + X-R-y + X-R-y + ...} \longrightarrow \text{X-R-Z-R-Z-R- . . .}$$

In the formula x-R-y, R is a bivalent radical, and x and y are functional groups capable of reacting with each other to form the known functional group e. Thus, if X is HO and Y is COOH, Z will be CO-O. The compounds x-R-y are called bifunctional compounds, and their reactions are bifunctional reactions. Reactions of the type x-R-x + y-R'-y product may be included in this class.

Bifunctional reactions present the possibility of following various courses:

a) They may be intramolecular at the first stage. The product will then be the cyclic monomer.

(R-Z)

b) Reaction may be intermolecular molecular at some subsequent stage. Cyclic polymer at the first stage and intra-molecular the product will then be a cyclic polymer

(-R-Z-) n

c) Reaction may be exclusively intermolecular. In this case, the product will be an open chain of the type X-R-Z-R-Z-R- . . . X-R-Z-R-Z-R- These possibilities may be illustrated by the hydroxy acids of the series H-O-$(CH_2)_n$-CO-OH. The self-esterification of these might lead to simple lactones [40].

O-(CH_2) n-CO

or to cyclic polyesters

O-(CH_2) n -CO

or to open chain polyesters

H(O-(CH_2) n-CO) p OH.

2.2. Polyurethanes.

In terms of production and use, polyurethanes (PUs) are a versatile class of polymers. They are excellent for a variety of applications due to their exceptional features. They are resilient, resistant to chemicals, and have excellent mechanical qualities. Because polyurethane has reactive capabilities in its main chain, it is more compatible with most polymers and can be used to create networked structures [41,42].

A unique class of polymeric materials known as polyurethanes (PUs) varies significantly from most other plastic kinds in many ways. They can be used in various products, including paints, liquid coatings, elastomers, insulators, elastic fibers, foams, integrated skins, etc. [43,44].

The absence of urethane monomers distinguishes polyurethane from other types of polymers. The most reactive moiety in polyurethane is the urethane (-NHCOO-) chemical bond, which is present in the polymer. The final product's nature, qualities, and applications vary depending on the raw components [45,46].

Basic polyurethane synthesis chemistry is simple; however, in a lab context, it becomes complicated. The complexity of the synthetic method is caused by the range of starting materials, additives, and catalysts. Polyurethanes are synthesized by the addition of alcohols and isocyanates. The diisocyanates react with the diols or polyols, constituting the alcoholic component. Since both ingredients are widely accessible, a wide range of polyurethanes can be produced. In the case of foams, PU can be soft; in the case of car parts, it can be rigid. In our daily lives, polyurethane can be found in various products, from footwear to bedding to roofing materials for homes, from automobiles to the building industry. They are everywhere in the things we do every day [47,48].

2.2.1. Types of polyurethanes, their properties, and applications.

Different types of polyurethanes are available according to their synthetic route and applications. Worldwide there are different types of PU production, with an estimated forecast up to 2020 given herein in Fig. 4. Fig. 5 illustrates the most important types of PUs and some common examples of their uses [49,50].

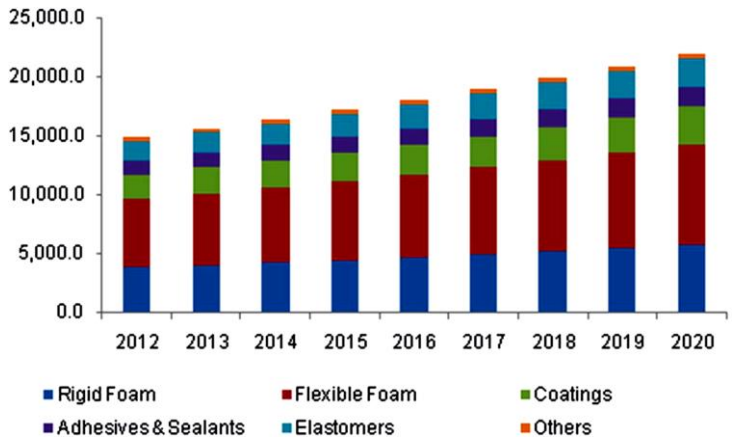


Figure 4. Worldwide PU production and an estimated forecast up to 2020.

2.2.1.1. Polyurethane foams.

PU foams are polyurethanes that are frequently found. Low-density flexible foams and low-density rigid foams are both types of polyurethane foams. Cushions, vehicle seating, and

other items made of furniture use low-density flexible foams. Flexibility, resilience, high mechanical strength, and durability are needed in these sectors. High mechanical strength, poor heat conductivity, limited moisture absorption, and low density are all characteristics of rigid foams. They are utilized as base materials in producing insulation panels for buildings and refrigerators [51,52].

By simply altering the types and quantities of the surfactants, catalysts, blowing agents, isocyanate, and polyol used in their production, as well as the degree of intercalation and exfoliation between the fillers and matrices to meet the desired purpose, PU foams can be easily customized to produce specific products [53,54].

One of the most well-known, adaptable, and energy-efficient insulating materials is rigid polyurethane foam. On the one hand, these foams can greatly save energy expenditures, and on the other, they can improve the comfort and performance of commercial and domestic appliances. Both petroleum-based polyols and bio-based polyols derived from plant lignin or vegetable oils can be used to create rigid PU foams. The type of hydroxyl group found in the polyols affects the qualities of the formulated PUs. For instance, glycerine, a polyol derived from petroleum, has a primary hydroxyl group [55,56].

On the other hand, polyols made from vegetable oils (like castor oil) have secondary hydroxyl groups. As a result, PUs made from these two types of polyols have differing mechanical and physical characteristics [57-59].

Additionally, the reaction between a polyol containing a secondary hydroxyl group and an isocyanate proceeds more slowly than the reaction between a polyol containing a primary hydroxyl group and an isocyanate. Therefore, a combination of primary and secondary polyols with hydroxyl groups is frequently employed to reduce the usage of polyols derived from petroleum [60,61].

For example, rigid PU foams with high physical and mechanical properties have reportedly been produced through a mixture of glycerine and castor oils.10 Moreover, the presence of different polyols may affect the physical properties of the PUs. For example, the presence of transesterified palm olein-based polyol, which contains a secondary hydroxyl group, can decrease the reactivity of the foaming profile of rigid PU [62,63].

The phase separations between the soft and hard segments of some block copolymers make flexible polyurethane (PU) (FPU) foams more flexible. Therefore, by purposefully manipulating the relative proportions of each of these segments, PU foams can be altered. They may be categorized as flexible PUs depending on a few physical traits, such as density, toughness, hardness, tearing resistivity, combustibility, surface elasticity, etc., where a combination of these traits can guarantee good flexibility in the PU compound. Flexible PU foams are used as padding for various consumer and business items, including carpet underlays, furniture, bedding, automotive interior parts, packaging, biomedicine, and nanocomposites [64,65].

There are typically two main phases in synthesizing flexible PU foams: blowing and gelling. The blowing process results in the production of carbon dioxide and urea, which expand and are entrapped by the reaction mixture. The isocyanate and hydroxyl groups of the polyol react to generate the urethane bonds. The degree of cross-linking following the reaction between the polyol and diisocyanate, the segmental movement of the urea group, how the polyol and urea interact, and other factors are some of the factors that determine the shape and microstructure of the PU foam [66,67].

2.2.1.2. Coatings, adhesives, sealants, and elastomers.

Using PUs as coatings, adhesives, sealants, or elastomers can lead to an expanding number of applications and profitable markets (CASE). This is due to the numerous great and adaptable mechanical, chemical, and physical qualities that PUs frequently display. While PU sealants can produce extremely tight seals, PU adhesives can offer good bonding qualities. A PU must have outstanding adhesive qualities, high chemical resistivity, excellent drying, -temperature flexibility, and sufficient scratch resistivity to be acceptable for coating applications [68,69].

For high-performance coating applications, several types of nanoparticles, such as titanium oxide and silicon dioxide, may occasionally be utilized to give the material anticorrosive qualities. This product's longevity might be increased, and its beauty could be enhanced. It is noted that although PU coatings are well suited to provide several desirable qualities, their inadequate impact resistance and sensitivity to UV deterioration, when used outside, can limit their application [70,71].

Vegetable oils were recently used to create eco-friendly adherent PU coatings using a green solvent technique (cotton seed and karanja oil). The physicochemical and thermal properties of the product were carefully examined. Even at an industrial scale, the material's adhesion, impact resistance, flexibility, and gloss results showed that it is suitable for coating applications [59,72,73].

From a PU and poly hydroxyl urethane hybrid, specific isocyanate-free innovative bonding and adhesive materials were produced. Additionally, it was discovered that this substance might replace Pus, made of isocyanates. Most typical adhesives used in sandwich materials, like wood composites and other sandwich materials, are based on phenol and urea-formaldehyde. They are frequently used as binders for interior and exterior solid wood and plywood components; however, it has been discovered that the discharge of organic solvents from them seriously compromises the integrity of the environment. It is discovered that they also play a part in industry's heavy reliance on petroleum use [74,75].

Research has recently focused on developing adhesives and other binders from renewable resources, particularly plant oils. This is based on their benefits to society, the environment, and the economy. For instance, jatropha oil has reportedly been found to have several benefits as an adhesive. This is because its gums contain oil and can be used to make adhesives based on renewable resources. In reality, additional literature papers have shown that PU wood adhesives have been successfully made from jatropha oil and that the glue has been discovered to have several extremely desirable qualities [76,77].

The glue made of jatropha oil is also recyclable, which makes it simple to use in adhesive applications. This raises the possibility of replacing traditional petroleum-based materials with them. Researchers have been interested in jatropha oil because of its low price compared to other oils like rapeseed and soybean, and particularly it is potential for use in wood adhesive applications. Other oils, such as palm oil, have also received much attention in addition to jatropha oil [78-80].

PU elastomers are another kind. They are inexpensive, resistant to heavy weights, strong under compression, and simple to synthesize and color. Rubber and plastic alternatives are thought to be polyurethane elastomers. They are highly impact resistant, have low moisture absorption, strong abrasion resistance, and chemical and solvent resistance [79,81].

They are useful for producing packaging materials in the health product business and the printing industry because of their superior mechanical qualities. Additionally, they are utilized in bushings, rollers, pulleys, shock absorbers, and wheels. The soles of shoes are made in the footwear industry using low-density elastomers. They can be made in various forms, colors, and patterns. They are lighter than metals and have desirable stress-recovery properties. They can also tolerate a variety of environmental conditions [82,83].

2.2.1.3. Thermoplastic polyurethanes (TPUs).

Segmented polyurethanes with alternating hard and soft blocks are known as thermoplastic polyurethanes (TPUs). During the synthesis, the length of the soft and hard blocks can be adjusted. They are extensively utilized in manufacturing footwear, power tools, sports equipment, and medical equipment. TPUs are highly abrasion-resistant, chemically and solvent-resistant, and oil and grease resistant [84,85].

Thermoplastic polyurethanes (TPUs) exhibit various physical characteristics and processing uses. They often resist impact, abrasion, and weather and are elastic and flexible. TPUs can be colored and made using a variety of fabrication methods. Therefore, using TPUs could increase many products' general durability [86,87].

Novel fatty-acids-based diisocyanates are used in the synthesis of TPUs, and it has been reported that the material produced has notable thermal stability at temperatures below 235 C without significantly losing weight. It has also been reported that hard renewable thermoplastics based on spiroacetal moieties were successfully synthesized, and the matching materials were made in a very high yield. Glass transition temperature for the product was determined by DMTA and DSC analysis to be approximately 85 C. Additionally, there was no discernible acid-mediated breakdown of the produced PU during the hydrolytic stability study [88].

A different study used dimer-fatty-acid-based diisocyanate and a few additional renewable diols to create entirely bio-based thermoplastic polyurethane (PU). The PU material was created using a one-step bulk synthesis technique and was discovered to be appropriate for coatings, automotive, construction, adhesives, and textile applications [89].

TPUs have also been successfully used in applications like polymer controllers for drug release in vaginal rings and medical tubing because their high mechanical properties could allow tubes with thin walls without necessarily incorporating a plasticizer. This is because TPUs are water-insoluble, non-ionic, and inert [90].

Thermoplastic polyurethanes are the most significant subclass of polyurethanes. The beginning material and qualities of this kind of material vary. The needed qualities can be met by synthesizing thermoplastic polyurethanes. They have good flexibility and clarity and resemble polymers [51,87].

2.2.1.4. Binders.

PU binders are frequently used to join various fiber types and other materials. A persistent bonding effect between organic materials and long-strand lumbers, oriented strand boards, laminated veneer lumber, medium-density fiberboards, particle boards, and straw boards is facilitated by PU-based binders. The hard-to-soft segment ratio of PUs should be high, and exceptional heat stability is needed as a binding material. For a high-quality binder, having a particular or moderate acid number (not too high or low), weak crystallinity, a small

molecular weight, and a restricted particle distribution (if PU dispersion) can be advantageous. It is also preferred to use hybridization with an acrylic polymer to give PU binders exceptional chemical resistance. The primary industries include sand casting, wood panel production, ink-jet printing, foundry industries, and elastomeric or rubbery flooring surfaces [91,92].

Among these, creating an oriented strand board represents the primary use of PU binders (OSB). These panels can be used for various manufactured housing applications, including shop panels, joist and beam construction, flooring, and structural sheathing. Additionally, the manufacture of rebonded foams, which are utilized as carpet underlay, primarily makes use of PU binders and other chemicals to glue flexible scrap PU foams to the carpeting underneath. The use of PU as a potential replacement for binders based on organic solvents has been suggested because of its superior binding capabilities [93,94].

2.2.1.5. Waterborne polyurethane dispersions.

Waterborne polyurethanes are a common name for coatings and adhesives that primarily employ water as the solvent (WPUs). The amount of permitted volatile organic solvents and other hazardous air pollutants that may be emitted into the environment is regulated by several laws. Therefore, polyurethane dispersions (PUDs), also known as waterborne polyurethane dispersions, are essential for most commercial and industrial applications (WPUDs) [95-97].

PUDs offer the special benefit that the viscosity of the dispersion is independent of the polymer's molecular weight. As a result, only the drying process can be used to manufacture high-solid-content WPUs (HSCWPUs). The polyurethane particles and the aqueous medium make up the two-phase colloidal dispersion. In the PU chain, several pendent acid or tertiary nitrogen groups are neutralized to form salts, essentially providing water dispersibility centers. Different characteristics of this dispersion are caused by the kinds and quantities of polyol, isocyanate, ionomers, and chain extender employed [73,98].

2.2.1.6. Polyurethane ionomers.

Polar urethane groups in polyurethane ionomers can interact with one another through hydrogen bonding. The ionic groups in the polyurethane ionomers can interact, agglomerate, and adhere to the hydrophobic region. A wide range of physical and mechanical qualities can be achieved by varying the molar masses of the segments, chemical structure, internal surfactants, degree of neutralization, and the ratio of the soft to the hard segments. The materials may be sticky and mushy, crumbly and rigid, or combined [99,100].

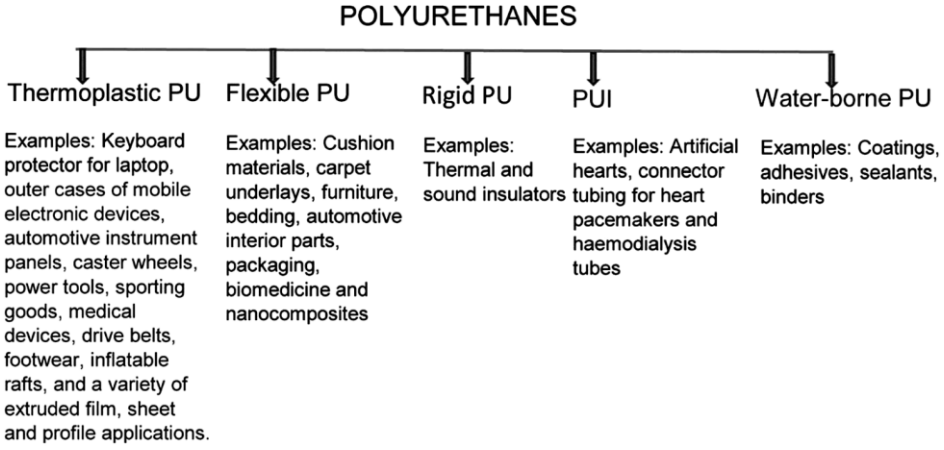


Figure 5. Important types of PUs and common examples of their applications.

2.2.2. Raw materials of polyurethane.

Generally, a chain extender, catalyst, and/or other additives are present when a di/poly isocyanate and a diol or polyol undergo a chemical reaction to generate repeated urethane groups. Along with urethane connections, ester, ether, urea, and aromatic rings are frequently found in the PU backbone [101].

2.2.2.1. Isocyanates.

Isocyanates are necessary building blocks for the production of PU. These are isocyanates with two or more -NCO groups per molecule, often known as di- or polyfunctional isocyanates. These can be aliphatic include cycloaliphatic, polycyclic, or aromatic including TDI, MDI, xylene diisocyanate (XDI), meta-tetramethyl xylylene diisocyanate (TMXDI), hydrogenated xylene diisocyanate (HXDI), naphthalene 1,5-diisocyanate (NDI), phenylene diisocyanate ((DBDI). Examples of several typical isocyanates are shown in Figure 4 [102].

The isocyanate group has a cumulated double bond sequence of R-N=C=O, and its reactivity is determined by the positive nature of the carbon atom (Scheme 1), which is vulnerable to attack by nucleophiles and to assault by electrophiles when it comes to oxygen and nitrogen(see Figure 6) [103].

The negative charge delocalizes into R if R is an aromatic group (Scheme 2), making aromatic isocyanates more reactive than aliphatic or cycloaliphatic isocyanates. Regarding aromatic isocyanates, the type of substituent also affects how reactive the isocyanate group is; electron-attracting substituents in the ortho or para position increase the reactivity while electron-donating substituents reduce it. The second isocyanate in diisocyanates attracts electrons, increasing the first isocyanate's reactivity. Para-substituted aromatic diisocyanates are more reactive than their ortho analogs principally due to the steric hindrance provided by the second -NCO functionality [104].

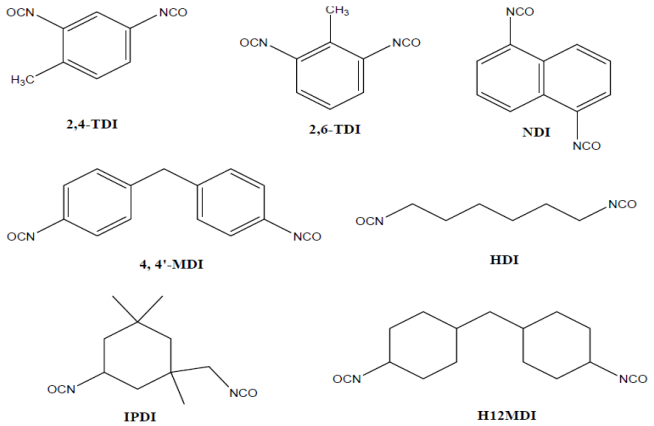
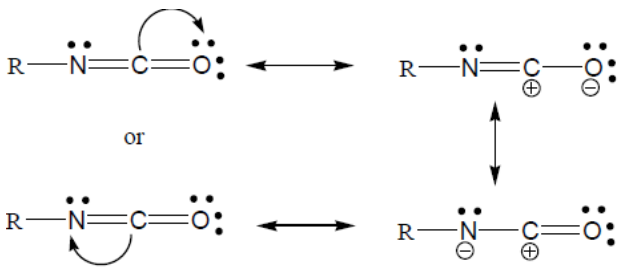
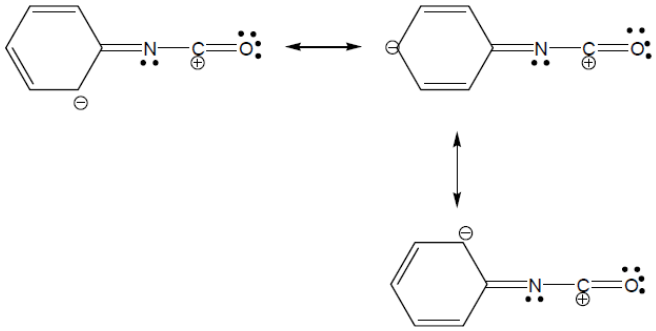


Figure 6. Common isocyanates.



Scheme 1. Resonance in isocyanate.

Based on the positioning of the -NCO groups, the two-NCO groups in isocyanates also have different reactivities relative to one another. For instance, the two -NCO groups in IPDI have different reactivities due to their different location points. Since the two isocyanate groups are not conjugated to the aromatic ring, TMXDI functions as an aliphatic isocyanate. Vinyl-terminated isocyanate is another isocyanate that is gaining popularity because, in addition to the -NCO group, the extra vinyl group also supplies sites for cross-linking (Figure 5) [105,106].



Scheme 2. Resonance in aromatic isocyanate.

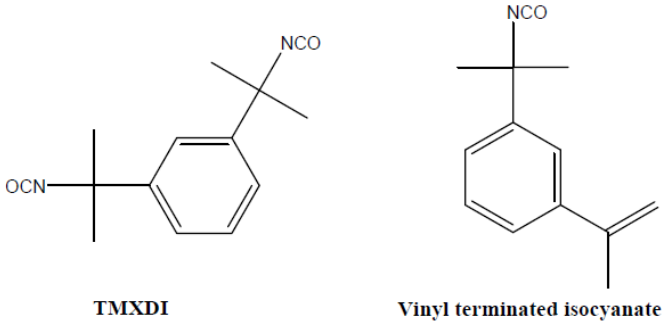


Figure 5. Other isocyanates.

TDI, HDI, IPDI adducts with trimethylolpropane (TMP), dimerized isocyanates known as uretdiones, polymeric MDI, and blocked isocyanates (where alcohols, phenols, oximes, lactams, and hydroxylamines are blocking agents) are polyisocyanates that are also utilized in the manufacturing of polyurethanes. To create completely biobased PU, fatty acid-derived isocyanates are synthesized using Curtius rearrangement. The qualities necessary for end-use applications determine which isocyanate is best for producing PU. The choice of aromatic isocyanates for preparing stiff PU results in PU with inferior oxidative and UV stabilities [107].

2.2.2.2. Polyols.

Spolyols are substances with a variety of hydroxyl groups. Along with hydroxyl groups, they may also have other functions, such as ester, ether, amide, acrylic, metal, metalloid, and others. The backbone of polyester polyols (PEP) is made up of both ester and hydroxylic groups. They are typically made by condensing ethylene glycol, 1,4-butane diol, 1,6-hexane diol, and a dicarboxylic acid/anhydride (aliphatic or aromatic) [108].

The degree of cross-linking and starting PEP's molecular weight has an impact on the characteristics of PU as well. A hard PU with good heat and chemical resistance is produced by highly branched PEP, whereas a flexible PU with good flexibility at low temperatures is produced by less branched PEP. Similarly, low molecular weight long-chain polyols result in inflexible PU, whereas high molecular weight long-chain polyols result in flexible PU. Castor oil is a superb illustration of PEP that occurs naturally. PEP is produced chemically by

converting additional vegetable oils (VO) because PEP contains ester groups, which makes them sensitive to hydrolysis and worsens their mechanical characteristics [109].

By adding a small number of carbodiimides, this issue can be solved. PEP is more expensive than polyether polyols (PETP). They are created through the additional reaction of ethylene or propylene oxide with starters or initiators that are alcohol or amine-based in the presence of an acid or base catalyst. Due to their high moisture permeability and low Tg, PU made from PETP is not widely used in coatings and paints [110].

Acrylated polyol (ACP), which is produced via free radical polymerization of hydroxyethyl acrylate/methacrylate with other acrylics, is another type of polyol. ACP creates PU with better thermal stability and infuses the final PU with typical acrylic properties. Applications for this PU include coating materials [111].

Metal-containing polyols or hybrid polyols are created by further modifying polyols with metal salts (such as metal acetates, carboxylates, and chlorides) (MHP). Good thermal stability, gloss, and anti-microbial properties are displayed by PU made from MHP. The literature cites numerous instances of VO-based PEP, PETP, ACP, and MHP employed as PU coating materials. Another illustration is the fatty amide diols and polyols formed from VO (explained in detail in chapter 20, Seed oil-based polyurethanes: an insight), which have made ideal building blocks for creating PU. Because the diol or polyol backbone of these PU contains an amide group, they have demonstrated good thermal stability and hydrolytic resistance [112].

2.2.2.3. Additives.

In addition to a polyol and an isocyanate, other additives might be needed for making PU, mostly to regulate the reaction, alter the reaction conditions, and finish or alter the finished product. These include colorants, chain extenders, fillers, moisture scavengers, catalysts, and crosslinkers. Catalysts are used in the synthesis of PU to encourage the reaction to occur at higher reaction rates, lower temperatures, deblocking blocked isocyanates, and lower deblocking and curing temperatures and times [113].

Alkali metal salts of carboxylic acids and phenols (such as calcium, magnesium, strontium, and barium salts of hexanoic, octanoic, naphthenic, and linolenic acid) as well as aliphatic and aromatic amines (for example, diaminobicyclooctaneDABCO), organometallic compounds (for example, dibutyltin dilaurate, and Tertiary amines' catalytic activity is influenced by both their structure and basicity; catalytic activity rises with more basicity and falls with steric hindrance on the nitrogen atom of the amine. Giving the electrons on the nitrogen atom of the tertiary amine to the positively charged carbon atom of the isocyanate facilitates the complex formation between amine and isocyanate, which catalyzes the reaction [114].

Metal catalysts bear superiority over tertiary amines because they are comparatively less volatile and less toxic. Metals catalyze the isocyanate-hydroxyl reaction by complex formation with isocyanate and hydroxyl groups. The positive metal center interacts with the electron-rich oxygen atom of both the isocyanate and hydroxyl groups, forming an intermediate complex, and by further rearrangement, formed of urethane bonds [115].

PU synthesis uses difunctional low molecular weight diols (ethylene glycol, 1,4-butanediol, 1,6-hexanediol), cyclohexane dimethanol, diamines, and hydroxyl-amines (diethanolamine and triethanolamine) as chain extenders and crosslinkers, respectively. Since isocyanates are excessively sensitive to moisture or water, even in minute amounts, moisture scavengers, such as oxazolidine derivatives and zeolite-type molecular sieves, are used to cut

off or eliminate the involvement of water during PU production. Blowing agents are used in the foaming process to create PU foams with cellular structures (e.g., hydrocarbons, CO_2, hydrazine) [116].

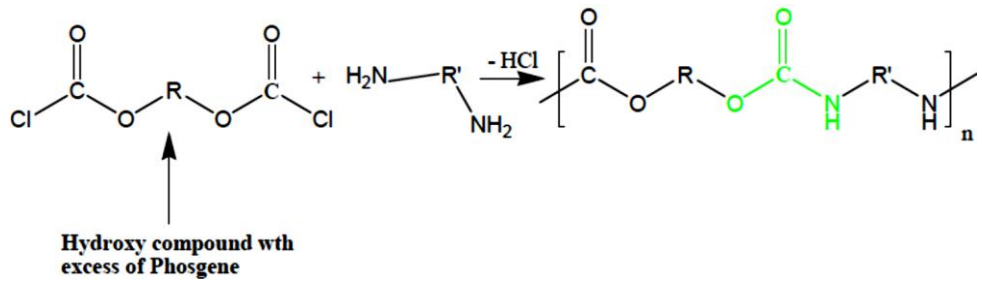
2.2.3. Chemistry of polyurethane.

PU are products of carbonic acid. They are known by their previous name, polycarbonate, which is an ester of a substituted carbamic acid. PU is created when

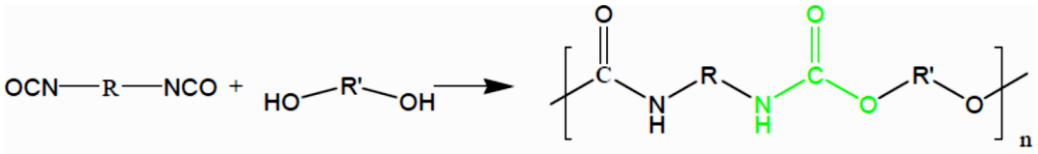
(i) the reaction between diamine and bischloroformates generates a condensation polymer (Scheme 3)

(ii) Polyfunctional or polyfunctional hydroxy compounds or other compounds with multiple active hydrogen atoms are added to diisocyanates to form a polymer (Scheme 4).

The latter process is more significant from an industrial viewpoint because no byproduct is produced [117].



Scheme 3. Reaction of bischloroformate with diamine.



Scheme 4. The reaction of a diisocyanate with di or poly hydroxy compound.

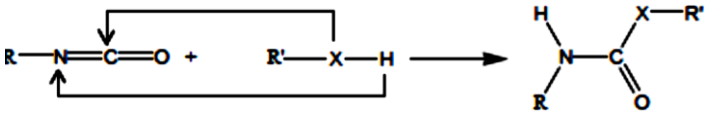
The isocyanate reaction allows for the production of custom polymeric goods ranging from rubber to fibers. The isocyanate reactions are often classified into two classes:

a) with a molecule containing active hydrogen, addition (primary and secondary and tertiary) reaction (Schemes 6, 7, and 8)

b) self-addition response (Scheme 9). CO_2 is emitted during several processes, which helps PU foams develop.

The fundamental isocyanate reaction (Scheme 10). At normal temperatures, molecules, including amine, water, alcohol, carboxylic acid, urethanes, and ureas that contain active hydrogen atoms react quickly with isocyanates, which have the structural formula R-N=C=O. (Scheme 5).

When a diisocyanate reacts with a diol, a linear PU is produced, while a branched or cross-linked PU is produced when a polyhydric molecule reacts (polyol). When a molecule with three or more isocyanate groups combines with a diol, the branched or cross-linked PU is also produced; nevertheless, the commercial relevance of this method is minimal [118].



Scheme 5. The reaction of isocyanate with active hydrogen compound.

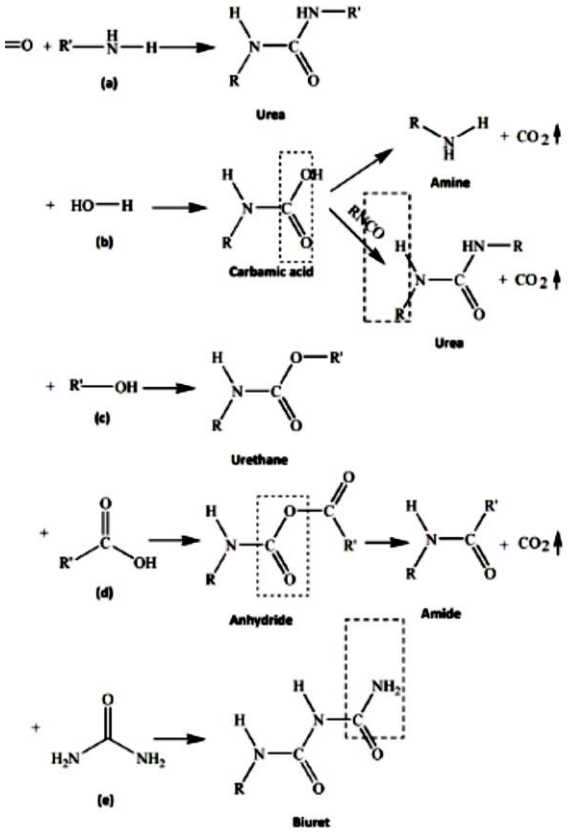
2.2.4. Mechanism.

The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as reactions with active hydrogen compounds [119].

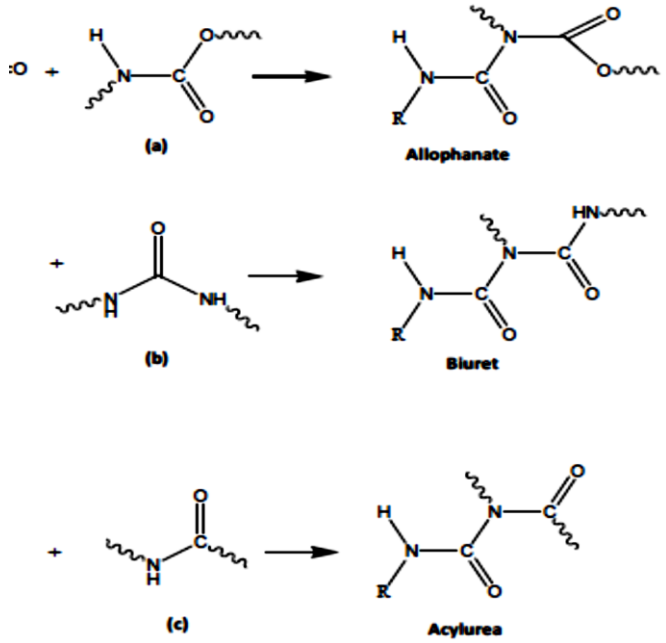
2.2.4.1. Reaction in the absence of a catalyst.

The active compound acts catalytically in the reaction as follows (Scheme 9). As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic center of the active hydrogen compound; hydrogen is added to the –NCO group. The reactivity of the –NCO groups is increased due to the presence of the electron-withdrawing groups and decreases by the electron-donating groups.

While the aromatic isocyanates are more reactive than the aliphatic isocyanates, the steric hindrance at –NCO or HXR groups reduce the reactivity. The order of reactivity of active hydrogen compounds with isocyanates in uncatalyzed systems is as follows: Aliphatic amines> aromatic amines> primary alcohols> water>secondary alcohol> tertiary alcohol> phenol> carboxylic acid> ureas> amides>urethanes [120,121].



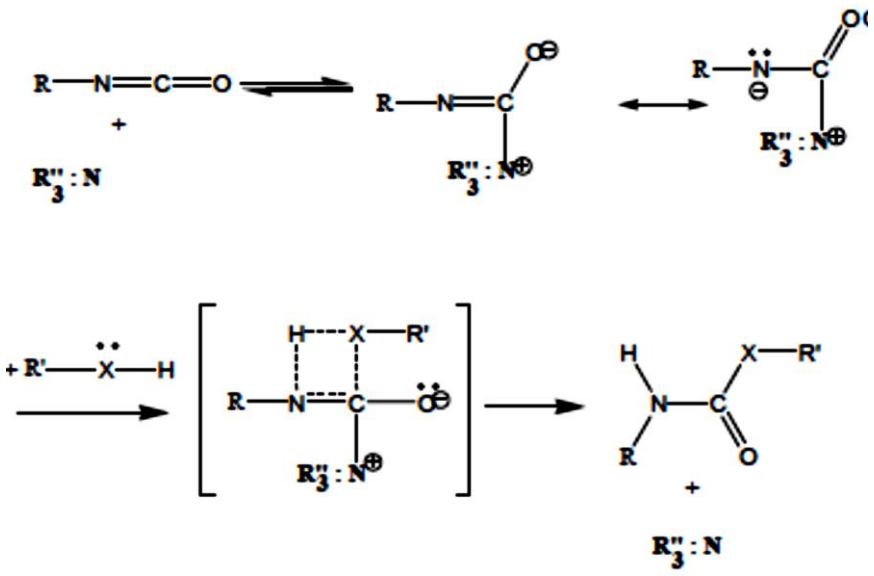
Scheme 6. Primary addition reactions of isocyanate with (a) amine, (b) water, (c) alcohol, (d) carboxylic acid, (e) urea.



Scheme 7. Secondary addition reactions mechanism of isocyanate with (a) polyurethane, (b) polyurea, and (c) polyamide.

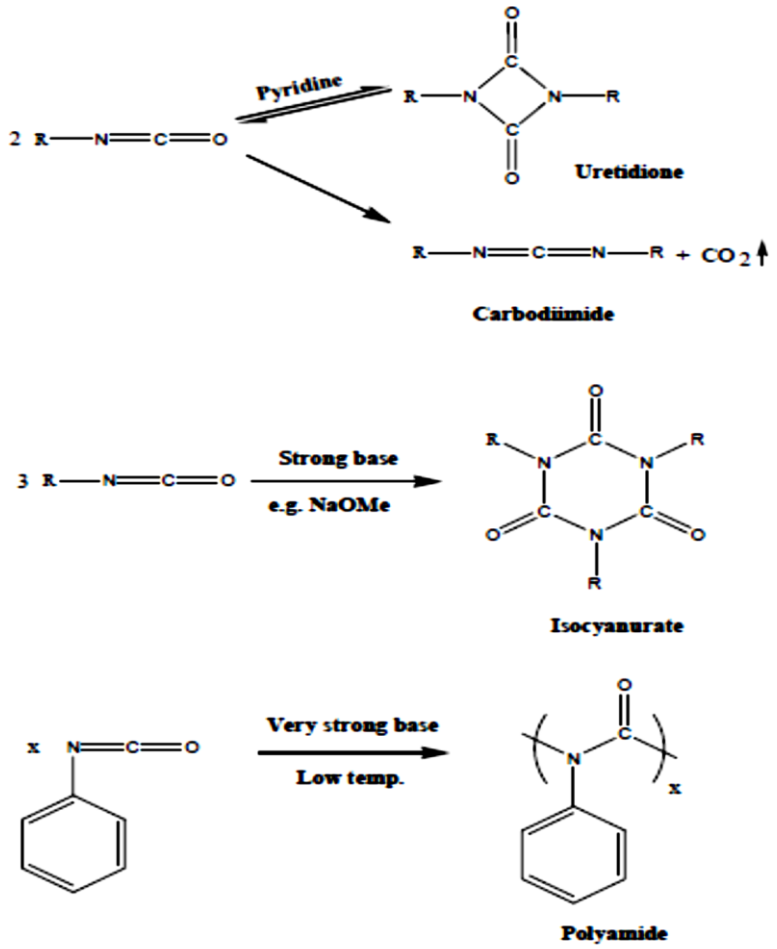
2.2.4.2. Reaction in the presence of a catalyst.

Additionally, the isocyanate reactions of class (a) are quite catalyzed. Different catalysts have varying degrees of influence on the different isocyanate reactions. Isocyanates are used in numerous industrial processes that use catalyzed reactions. The most frequently zed catalysts for the reaction are tertiary amines, and metal compounds like tin compounds (as described before in the chapter) (Schemes 10 and 11). Similar to the uncatalyzed reaction, the mechanisms (Scheme 9). The reaction is catalyzed as follows by tertiary amines and metal salts:

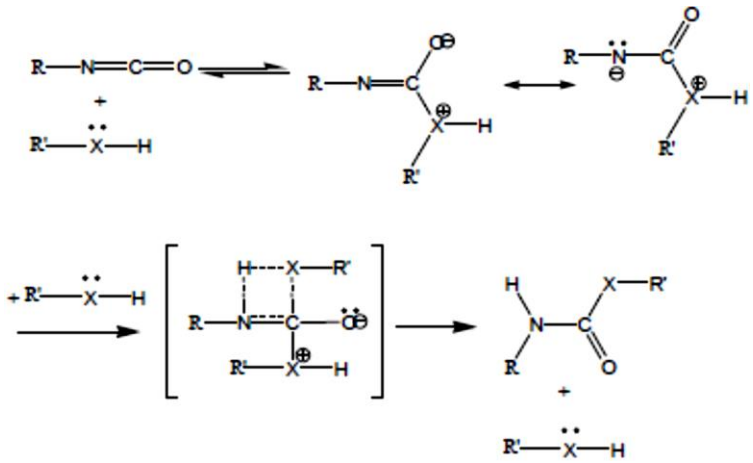


Scheme 8. Tertiary amine catalyzed reaction.

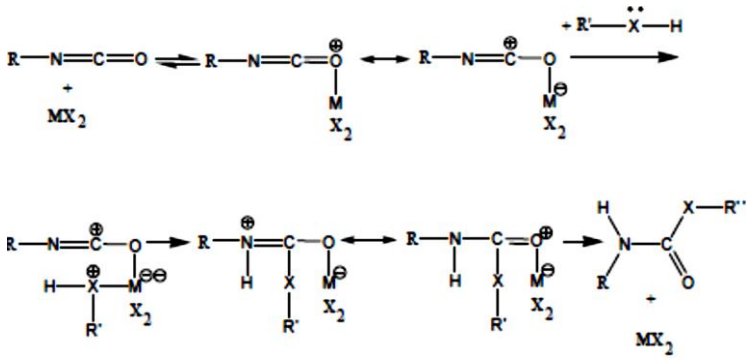
Except for situations when steric hindrance is overt, the catalytic activity of amines closely tracks their base strength. In contrast to metal salt compounds, which typically have less impact on these reactions and are especially ineffective catalysts for self-addition reactions, this catalyst is also effective for those processes [122].



Scheme 9. Self-addition reactions of isocyanate.



Scheme 10. Isocyanate reaction in the absence of a catalyst.



Scheme 11. Metal salts catalyzed reaction.

2.3. Polyurethane applications in finishing textiles.

Aqueous dispersions of WPUs, one of the PU kinds, have been extensively used in textile applications. Waterborne polyurethanes are less toxic and more environmentally friendly than their solvent counterparts because they don't contain any hazardous volatile organic compounds. They also exhibit wonderful qualities, including permeability, abrasion resistance, and suppleness (soft-to-touch surface). Additionally, using WPU as a finishing agent may greatly enhance the fracture resistance, washing resistance, and soap resistance of reactive dyes, acid dyes, and direct dyes on dyed fabrics [123].

Additionally, WPU coatings have excellent weathering resistance, water resistance, pH stability, low-temperature flexibility, improved solvent resistance, and favorable chemical and mechanical properties. UV quenchers or absorption groups were added to the polyurethane dispersions to enhance the fabrics' washing fastness and UV protection. This was accomplished by greatly increasing the UV dyeing protection of the cotton garments by employing N, N-dimethyl allyl p-benzoyl benzyl ammonium bromide as the UV absorber [124].

Hyper-branched polyurethanes (PUs) exhibit intriguing characteristics like high solubility, reactivity, and good rheological behavior because of their many end groups, compact molecular structure, and decreasing chain entanglement. By adding nanoparticles like Ag, Cu, TiO_2, SiO_2, and many others, WPU coatings' reduced stiffness and mechanical strength can be improved. To improve the flame resistance of WPU coatings, fire retardants, typically phosphorous, are introduced into the WPU structure [125].

Low molecular weight chitosan utilized in polyurethane dispersion for chain extension has also been researched. It was utilized to increase the stiffness, pill resistance, and mechanical strength of plain weave poly-cotton fabric pieces of various qualities. The same applies to fabrics made of pure cotton and wool. By creating an emulsion out of a silicon fluid that is often used as a fabric softener and adding an aqueous dispersion of polycarbonate diol with isopropyl alcohol as a co-solvent, Mazzon *et al*. attempted to make the silicon fluid hydrophobic. With 1.5 m particles and a remarkable water contact angle surpassing, the emulsion was stable [126].

In a two-step synthesis procedure, Farah Naza *et al*. created a series of waterborne polyurethanes based on chitosan using emulsion polymerization. The pre-polymerization step involved the use of hexamethylene diisocyanate, polyethylene glycol with a molecular weight of 6 kDa, and dimethylol propanoic acid to create isocyanate-terminated polyurethane A variable mole ratio of chitosan was used to prolong the polyurethane pre-polymer. The aqueous polyurethane with chitosan as a base and the monomers' Fourier Transform Infrared spectrum [127].

The structure-property link of the synthetic materials is perfectly corroborated by the results. In light of this, it can be said that WPU emulsions based on chitosan that have antibacterial qualities are good candidates for the textile finish. These types of finishes can prevent infectious problems by preventing pathogenic biofilm formation on materials. This research can be expanded to assess the performance of different textiles, such as wool or pure cotton [128].

A balance between water vapor permeability and water resistance is necessary for waterborne Pu-coated waterproof breathable fabric, which is accomplished by tailoring hydrophilic and hydrophobic segments. Due to its hydrophilic character, the poly (ethylene glycol) (PEG) segment has historically been used as a hydrophilic soft segment to provide high

WVP during PU synthesis. This hydrophilic PU lowers water resistance while increasing water vapor penetration [129].

A higher molecular weight of PEG in the soft segment increases the WVP of WBPU-coated nylon fabrics due to its increased hydrophilicity, according to research by Yen *et al*. on the composition of polycaprolactone-poly (ethylene glycol)-polycaprolactone (PCL-PEG-PCL) triblock copolydiol soft-segment [130].

When used as a textile coating, WBPUs made from hydrophobic poly (tetramethylene ether glycol) (PTMEG) and polypropylene glycol (PPG) 2050 (a copolymer of ethylene oxide and propylene oxide with OH end groups) achieved a balance of WVP (910-990 g/m2 x 24 h) and waterproof properties (>10,000 mm H_2O). The fabric's breathability is influenced by several other elements in addition to hydrophilic and hydrophobic ones, including the type of PU dispersions, coatings, additives, and processing conditions [131].

Initially, when PU was found to be a good fit for clothing, PUs were made into thin threads and mixed with nylon to create lightweight, flexible clothing. PUs have recently undergone technical advancement to produce thermoplastic elastomers and better spandex fibers. A wide range of PU-based leathers, bra cups, and synthetic skins can now be produced by manufacturers thanks to improvements in PU production techniques. These materials can also be utilized to make a variety of sportswear and accessories [132].

2.3.1. Textile application of SMPU.

SMPU can be created as fibers (macro, micro, and nanofibers), solutions, films, and foams for applications in non-woven materials, coatings, finishing, laminating, weaving, and knitting in the textile and apparel industries. The manufacture of SMPU fiber involves several techniques, including wet spinning, melt spinning, dry spinning, and electrospinning [133].

Laminated smart fabrics can use shape memory foams and films in various ways. Waterproofing, water vapor permeability (WVP), seam stitching, wrinkle recoverability, and crease fixing are some of the purposes of SMP films used on textiles. Due to its high WVP sensitivity, SMPU has the potential to produce breathable fabrics [134].

Jeong *et al*. studied the WVP properties of SMPUs, and breathable fabrics were invented by coating the SMPU membranes on a fabric substrate. Mondal and Hu also designed SMPU-coated fabrics, which abruptly increased WVP properties at room temperature (Tr) compared to low temperature. These results suggested that breathable textiles require a high WVP at higher temperatures and a low WVP at lower temperatures. Additionally, Mondal and Hu incorporated a small percentage of carbon nanotube in SMPUs and then coated it on cotton. They reported that the fabricated cotton fabric provided excellent UV protection, a required WVP and wearing coziness [135].

In addition to that, Chen *et al*. also investigated adjusting the size and shape of the free-volume holes in a fabricated membrane to control the WVP by adjusting the temperature. Further, Mondal and Hu attempted to find the influence of hydrophilic groups and crystalline soft segments on the WVP of SMPU films. They found that the WVP increased with the increase of PEG due to the enhancement of hydrophilicity. However, PCL or polytetramethylene glycol-based SMPUs have low WVP because of the increased interaction among the polymer chains [136].

A fabric-based thermoelectric generator was also created by Hu *et al*. utilizing a coating of aqueous PU composite on yarn. They claimed that this coated cloth's thermoelectric performance and processability were satisfactory. Additionally, SMPU is used to create

medical stockings that are used to treat persistent venous problems. This SMPU-based stocking enables management or control of the pressure applied when it is wrapped, and it also generates additional pressure (up to 50%) merely by heating the stocking. This kind of stocking has a strong chance of surpassing the limitations of traditional stockings. When compression therapy is administered, it can be used as a smart wound-care solution. SMPU is also used to create self-healing fabrics. Hu *et al*. created stimuli-responsive fiber utilizing SMPU in this situation, and it demonstrated 94% healing efficiency [137].

Because its WVP is sensitive to changes in temperature and humidity, shape memory PU has emerged as a promising candidate for coating nonporous fabrics with a breathable material. Water vapor-permeable fabrics were created by coating shape memory PU membranes on them after Jeong *et al*. study of the WVP characteristics of shape memory PUs with an amorphous reversible phase in 2000. The Tmtype shape memory PU with a semicrystalline reversible phase also produced smart WVP [138].

Shape memory PU-coated fabrics with a customized responsive room temperature were reported by Mondal *et al*. They also evaluated its WVP characteristics, which rapidly increased at the transition temperature. These findings demonstrate that breathable textiles with memory polymer coatings exhibit high WVP at higher temperatures and low WVP at lower temperatures (Fig. 7). The coated cotton fabric also demonstrated outstanding UV protection combined with good WVP and wear comfort by using shape memory PUs that contain a small number of multiwall nanotubes [139].

Chen *et al*. also described an effort to modify the size and form of the free volume holes present in membrane materials in addition to temperature-responsive WVP. Mondal *et al*. examined the effects of hydrophilic groups and soft crystalline segments on the WVP of shape memory PU-coated film. Due to the increasing hydrophilicity, the WVP increased as PE glycol concentration rose. However, due to enhanced contact between polymer chains, poly(caprolactone) glycol lowered WVP in the polytetramethylene glycol-based shape memory PU [140].

A technique for providing breathable clothes is made possible by fabrics covered with changeable WVP film. These textiles can be used for various things, including sportswear, footwear, gloves, and socks, thanks to the superior WVP of shape-memory polymers combined with microporous coatings. Liu *et al*. investigated a chemical modification method for cotton through shape memory finishing and coating. The resultant cotton fabric with Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy revealed that when shape memory PUs are grafted onto the cotton surface, high washability and enduring anticreasing of the treated cotton would be achieved [141].

Hu *et al*. found that coating various shape memory fabrics with shape memory PU resulted in the recovery of wrinkles, retention of creases, and preservation of patterns (Fig. 7), and they also created appropriate testing procedures for these shape memory fabrics.

Furthermore, Hu developed shape memory treatment agents for wool. Wool fabrics' thermal and hygrothermal effects were studied through shape memory finishing and coating with shape memory PU. The results confirmed that synthetic shape memory polymers influenced wool fabrics' thermal and hygrothermal behaviors [142].

When compared to shape-memory fabrics knitted or woven using shape-memory fibers, the transfer of shape-memory effects to the fabric during the finishing and coating process may be accomplished with a much smaller amount of shape-memory polymer, which is extremely effective. A fabric coated with shape memory PUs can achieve a variety of intriguing

capabilities, including antipilling, flexibility/strength protection, dimensional stability, shrink-proofing, a good flat appearance, crease retention, simplicity of 3D pattern design, and bulging recovery [143].

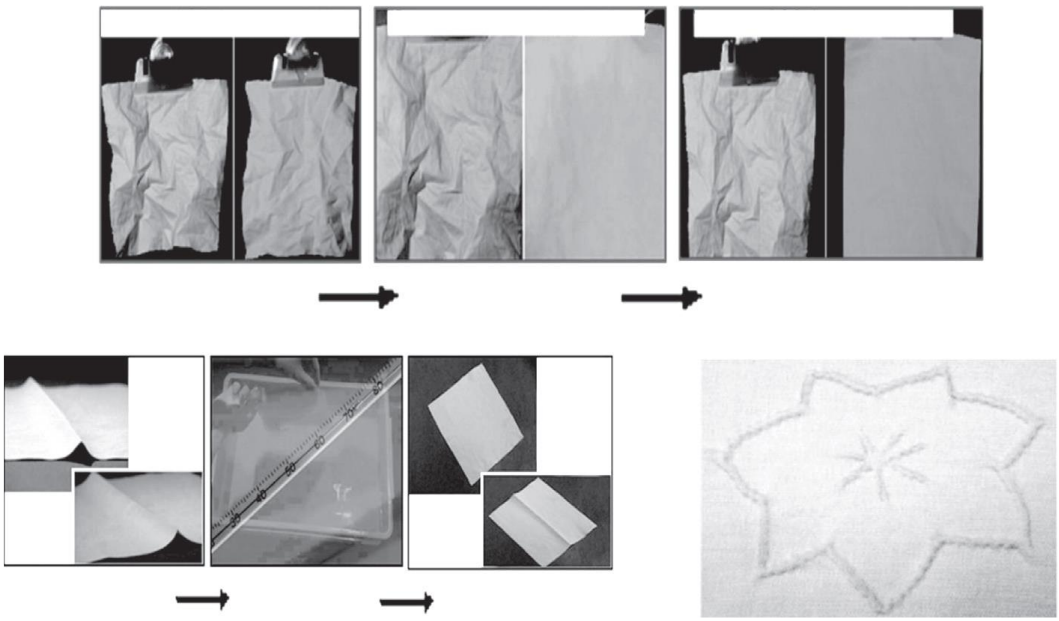


Figure 7. Memory coating for aesthetic appearance: (a) Flat appearance memory; (b) crease memory; and (c) pattern memory.

3. Summary

One of the most popular, adaptable, and extensively studied materials worldwide is polyurethane (PU). They are appropriate substitutes for metals, plastics, and rubber in many engineered items because they have the strength, hardness, and durability of metals combined with the elasticity of rubber. They have been used to create a wide range of products, including paints, liquid coatings, elastomers, hard insulations, elastic fibers, soft, flexible foams, and even complete skins. They are incorporated into many forms of industrial machinery. Diisocyanates of all kinds, different polyols, and other chain extenders and cross-linking substances can all be used to make PUs. This makes it feasible to obtain a wide variety of custom materials that can be used for numerous different applications. Most polyols initially utilized to make PUs came from petroleum sources. Still, the high cost, energy requirements, and environmental concerns have increased the need for a more acceptable and environmentally friendly replacement. Therefore, the most recent developments in PU-based materials/coatings for smart materials and functional textiles are presented and discussed in this study.

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Conflicts of Interest

The authors declare no conflict of interest.

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