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# A Review of Polyurethanes

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*Polyurethane*

**ABSTRACT:** Polyurethanes are used in almost every aspect of our everyday lives and have advanced areas including construction, medicine, automotive, marine, and apparel. Rigid and flexible polyurethane foams, rubbers, thermoplastic polyurethanes and many more are in everything from our couches, car steering wheels, even the soles of our shoes. This literature review is to discuss the discovery of polyurethane chemistry, today's uses, and advancements.

## Introduction

### Historical Background

Polyurethanes (PU) are a class of block copolymers formed by organic constituents, connected through urethane linkages. PUs were first discovered by Dr. Friedrich "Otto" Bayer [1] at IG Farben in 1937 Leverkusen, Germany. Bayer took inspiration from previous work by Wallace Hume Carothers' on polyamides and polyesters [2]. Bayer synthesized the first polyurethanes by condensing difunctional hexane diisocyanate and 1,4-butanediol monomers. The intended use of polyurethanes was to serve as an alternative to natural rubber and aircraft coating for World War II (WWII) [3]. Polyurethane became a cheap alternative to rubber during WWII and PU coatings were implemented in mustard gas resistant garments and high gloss airplane finishes, due to polyurethane's chemical and corrosion resistance [4].

Polyisocyanates (Figure 1) became commercially available in 1952, while Bayer continued to develop different polyester and polyisocyanates [5]. In 1956 DuPont had introduced Poly (tetramethylene ether) glycol (PTMG) (Figure 2) as the first commercially available polyether polyol [5].

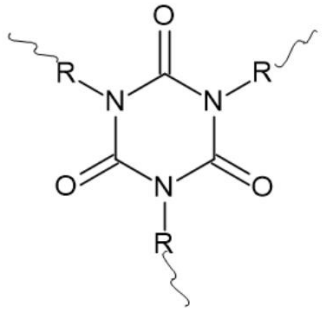

**Figure 1:** Structure of polyisocyanates.

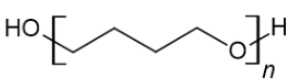

**Figure 2:** Structure of poly (tetramethylene ether) glycol.

The United States continued to make significant progress in the polyurethane field as BASF and Dow Chemical produced polyalkylene glycols in 1957 based on PTMG and 4,4'-diphenylmethane diisocyanate (MDI). By 1969 polyurethane reaction injection molding (RIM) was introduced and led to high performance polyurethane material, which led to the United States' first plastic body car in 1983 [5]. Polyurethanes have led to the advancements of many fields due to their versatile nature.

### Polyurethane Chemistry

Polyurethanes are a class of block copolymers characterized by the repeating urethane group which was produced from the step-growth reaction of a diol/polyol and a diisocyanate (Figure 3) in the presence of a chain extender.

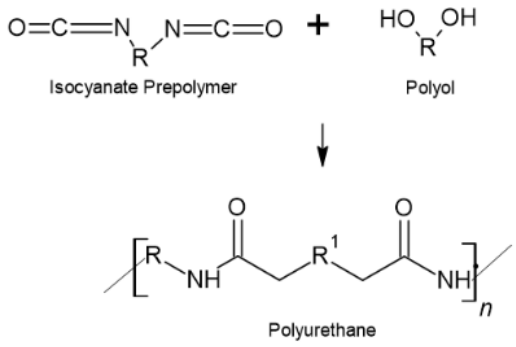


**Figure 3:** Diisocyanate and polyol reaction to produce a polyurethane.

The polyol forms the long chain length soft segments, illustrated in Figure 4, which provide more mobility and flexibility to the polyurethane. The isocyanate and chain extender form the hard segments in the polyurethane, as shown in Figure 4. Isocyanates are typically short chain molecules and show higher crystallization, which allows for tough and compact hard segments in the polyurethane. This combination of

hard and soft segments is what makes polyurethane a very versatile polymer.

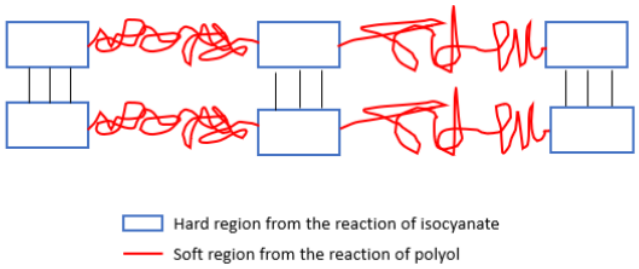


**Figure 4:** Visual representation of the hard and soft segments in a polyurethane.

Types of Polyurethane

3.1 Rigid Foams

Rigid PU foams are one of the most common insulation materials. The U.S Department of Energy reports show that one of the major energy consumers in homes is heating and cooling [6]. Polyisocyanate and PU foams are used by builders in residential and commercial buildings to reduce noise and ensure a stable temperature. These polymer foams are also used in refrigeration, window, and roof insulations [3]. Rigid PU foams can be developed through several synthesis routes. However, this highly crosslinked, closed-pore material is typically made by treating polyether or polyester polyols with polymeric MDI.

3.2 Flexible Foams

Flexible PU foams have become the standard for making furniture cushions, carpet underlays, bedding, automotive interior parts, mattresses, and many other applications. The phase separations between the soft and hard segments allows for the high flexibility of this block copolymer [7]. The synthesis route of flexible PU foams is very similar to that of rigid PU foams. However, different ratios of reagents produce carbon dioxide and urea that expand and then are trapped by the reaction [8].

3.3 Thermoplastic Polyurethanes

Thermoplastic polyurethanes (TPU) are typically flexible, elastic, and yield high resistance to weather, impact, and abrasion. The fabrication of TPUs has a wide range of techniques but when incorporated into other products, improves the durability of the product [9]. TPUs are melt processable and can be extruded, blown, compressed, and injection molded [10]. TPUs are most recognizable in applications for automotives, footwear, and construction [11].

3.4 Coatings

In order to use PUs for coating and adhesive applications, testing must be conducted to show good potential adhesive properties, excellent drying, scratch and chemical resistance, and low temperature flexibility [12]. PU coatings can belong to one of five ASTM classifications: oil modified, moisture cure, blocked, prepolymer plus catalyst, or two components [12]. Oil modified coatings are the reaction product of drying oils and are cured by oxidation of the unsaturated oils. Moisture cure uses terminal isocyanate groups that can react with ambient water to create a crosslinked polymer film.

Blocked curing uses a blocking agent that requires a higher temperature to unblock the isocyanate and allow crosslinking of the urethane. Prepolymer plus catalysts are like moisture cures but require a separate catalyst to accelerate the cure. Two component cure uses isocyanates and low molecular weight polyols to form adducts. Polyols are used to obtain extension and curing.

Advances in polyurethane applications

Polyurethanes have proven to be applicable to a variety of fields including construction, automotive, marine, coating, medical, apparel, and many others. The base of industry applications for polyurethanes has grown in the last 50 years and is driven by the production economics of the raw material and the market diversity of hard plastics, adhesives, and paints [13 Vantage Market Research reports that the Global Polyurethane Market was valued at 71.7 billion USD in the beginning of 2021 and ended the market is expected to surpass this by 91.2 billion USD by 2028 [14]. Figure 5 shows the Global Polyurethane market size at the end of 2021.

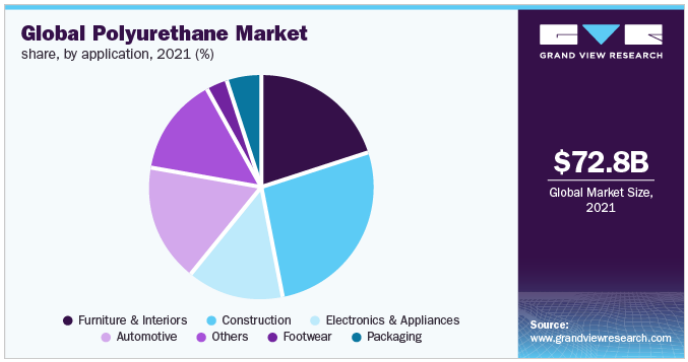


**Figure 5:** The US PU market size according to Grand View Research [15].

4.1 Building and construction

Polyurethanes are seen not only in insulation materials but in adhesives, coatings, flooring, forklifts, fire protective foams, and the safety gear used. PU adhesives and sealants are water resistant, similar to a strong glue, and resist UV light deterioration, which allows protection against natural elements [16]. Durable, heat resistant PU machine parts are used more frequently due to supply chain issues with metal. [17]. PU floor coating has recently been taking over for epoxy coating due to PUs high chemical resistance, high abrasion resistance, moisture resistance, high UV stability, and thermal shock resistance [18].

4.2 Automotive

Polyurethane products have been well-established in the automotive world since the 1960's [19] before the plastic body car in 1983. PUs can be found in the seating, interior padding, impact resistance front bumpers, steering wheels, mirror

surrounds, door panels, sunroofs, and many other vehicle components [20], [21], [22]. When using polyurethane materials as opposed to chrome or acrylics, the weight of the car is reduced drastically and increases the fuel economy which in turn makes the car more performance efficient [3].

### 4.3 Marine

Polyurethanes and epoxy have been used to advance marine technology to build and coat. PU epoxy coatings have shown to protect from corrosion, and water erosion. PU foams are used in boats for insulation, noise controlling, and damping properties, like that of the automotive industry. Recently researchers have studied using cyclodextrin based polyurethanes as a removal media for organic substances from water [23]. One study showed cyclodextrin based polyurethanes were able to successfully remove dyes like crystal violet and aniline blue from laundry water waste [24]

### 4.4 Medical

Polyurethanes are used in medical appliances like hospital bedding, catheters, tubing, and many other applications due to cost efficiency, good mechanical properties like toughness and longevity, and biocompatibility [25], [26]. PUs have also been shown to be effective in short term implants and as auxiliary materials in orthopedics [27]. Viscoelastic polyurethane foams were used as socket liners for prosthetics to provide more comfort and ease to amputees compared to the previous silicone liners.

### 4.5 Apparel

Thermoplastic polyurethane has taken over a large percentage of the fashion industry due to the high durability, comfort, waterproof, and moisture permeability [28]. PU was originally intended to be an alternative rubber and was then made into small threads to be incorporated with Nylon to create light and stretchable clothing. However, PU is used in shoes, bra cups, bathing suits, wet suits, windbreakers, rain jackets, and many other apparel items. PU has proven to be one of the more durable options for shoe sole as seen in Figure 6. PU adhesives and coatings are also widely used in the shoe industry to improve durability and appearance of shoe upper made of real and synthetic leather [20].

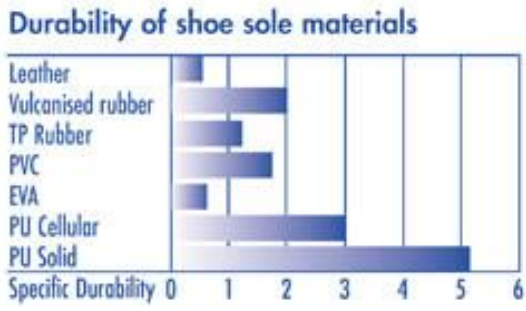


**Figure 6:** Comparison of different shoe soles according to the ISOPA – European Diisocyanate and Polyol Producers Association [29].

### Conclusion

Polyurethanes are seen in many aspects of our everyday life. We wear PU enhanced products on our feet, in our cars, in our furniture, and even on our floors. Polyurethanes have come a long way since their creation in 1937 and continue to progress.

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