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An overview of advances in methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) based polyurethanes: Chemistry, properties, and applications

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ABSTRACT

Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) remain the dominant aromatic diisocyanates used to produce polyurethanes (PUs), a class of polymers with unparalleled versatility spanning foams, elastomers, coatings, adhesives, and specialty materials. This review synthesizes the literature (with emphasis on the last ~7 years) to present: (1) the core chemistry of MDI- and TDI-based polyurethane formation and modern synthetic/processing variants (prepolymers, blocked isocyanates, latent systems); (2) structure–property relationships arising from hard/soft segment microphase separation, crosslink density, and formulation additives; (3) major advances in high-performance formulations including thermoplastic polyurethanes (TPUs), nanocomposites, and dynamic/dissociative networks (vitrimers) that enable reprocessing and self-healing; and (4) sustainability trends - bio-based polyols, non-phosgene and greener isocyanate routes, and chemical recycling strategies. This review highlights key enabling chemistries (transcarbamoylation, urethane exchange, glycolysis-derived feedstocks), summarizes representative performance gains from nanofillers and modified formulations, and discusses technological challenges for scaling sustainable and recyclable PU systems. Finally, recommendations are offered for research directions that are likely to accelerate the adoption of circular, lower-toxicity MDI/TDI-based PUs across major application sectors.

1. Introduction

Polyurethanes (PUs) are synthesized predominantly by the reaction of di- or polyisocyanates with polyols, producing urethane (carbamate) linkages. From an organic chemistry perspective, this transformation represents a classical nucleophilic addition, in which the hydroxyl group of the polyol attacks the electrophilic carbon of the –N=C=O moiety, yielding highly stable carbamate bonds. This reaction is remarkably versatile, as the reactivity can be fine-tuned through the choice of diisocyanates (aromatic vs. aliphatic), polyols (polyether, polyester, polycarbonate, or bio-derived), and catalysts (organometallic vs. organocatalysts). The result is a polymer family with properties ranging from soft and elastic to rigid and glassy, enabling applications across consumer, industrial, and biomedical sectors [1-3].

The origins of polyurethane chemistry date back to the pioneering work of Otto Bayer and co-workers in the late 1930s, who first demonstrated the potential of isocyanate–polyol chemistry as a platform for high-performance polymers. Over subsequent decades, industrial-scale production of diisocyanates was developed, enabling PUs to expand into coatings, adhesives, foams, elastomers, and composites. Among the numerous diisocyanates synthesized, aromatic species rapidly became dominant due to their combination of high reactivity, excellent performance in hard segment formation, and economic feasibility [4-6].

Within this class, methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are by far the most significant. TDI, generally used as a mixture of 2,4- and 2,6-isomers, is prized for its volatility, rapid reactivity, and ability to form flexible foams with open-cell morphologies, which dominate furniture, bedding, and automotive seating markets.

MDI, particularly in its polymeric form (pMDI), offers lower volatility, greater functionality, and enhanced rigidity, making it indispensable in rigid foams for insulation, construction, and appliance applications

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(Figure 1). Both diisocyanates, however, share the advantage of being cost-effective and available at large scale, derived from petrochemical feedstocks such as aniline, formaldehyde, and toluene [7-10].

Globally, the PU industry continues to expand, driven by demands for lightweight materials in automotive and aerospace sectors, energy-efficient insulation in buildings and appliances, and advanced elastomers in electronics and healthcare. Recent estimates indicate steady growth in MDI and TDI consumption, with major producers (e.g., BASF, Covestro, Wanhua) investing heavily in new production capacity.

At the same time, sustainability pressures - including concerns over isocyanate toxicity, environmental persistence of PUs, and reliance on fossil feedstocks - are reshaping research and industrial priorities. The challenge is thus twofold: to exploit the remarkable versatility of MDI- and TDI-based PUs while innovating toward greener, safer, and more recyclable systems [11, 12].

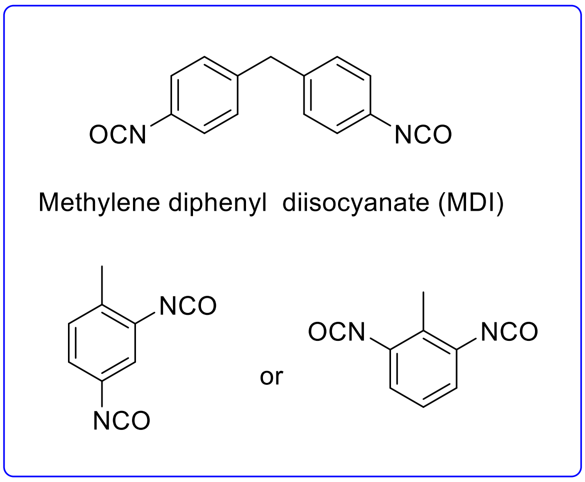

Fig. 1. Molecular structures of the two main aromatic diisocyanates used in polyurethane synthesis: methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI).

From a mechanistic standpoint, MDI and TDI represent model systems for studying the reactivity of aromatic isocyanates [13, 14]. Their electrophilicity is strongly modulated by resonance and inductive effects of the aromatic backbone, while their regioisomeric substitution patterns dictate differences in steric accessibility and relative reaction rates of the two –NCO groups.

For example, in 2,4-TDI the para –NCO group reacts more rapidly than the ortho group, a feature exploited industrially to control polymerization kinetics and foam morphology. In MDI, the symmetrical 4,4′-isomer promotes linear hard-segment packing and strong hydrogen-bonding interactions, while polymeric MDI offers multifunctionality that enables high crosslink densities.

These subtle electronic and steric effects illustrate the intimate connection between small-molecule organic chemistry and the emergent macroscopic properties of polyurethane networks [15, 16].

This review synthesizes recent advances (with emphasis on the past decade) in MDI- and TDI-derived PUs. It examines their structural and electronic features, mechanistic aspects of urethane formation and side reactions, structure–property relationships, and the breadth of their applications. Special emphasis is placed on emerging areas - such as bio-based feedstocks, dynamic covalent networks, nanocomposites, and biomedical formulations - as well as health, safety, and regulatory considerations that define their industrial future.

By framing these developments through the lens of organic chemistry, the review aims to highlight how molecular-level design dictates macroscopic performance and how innovative synthetic strategies can address the pressing challenges of sustainability and circularity.

2. Organic Chemistry of MDI and TDI

2.1. Structural features, resonance, and isomerism

TDI consists of two principal aromatic isomers: 2,4-toluene diisocyanate and 2,6-toluene diisocyanate. The positional difference in –NCO substitution strongly influences their relative reactivity.

In 2,4-TDI, the para-isocyanate group is more accessible and electronically activated, while the ortho-substituted group experiences steric hindrance, lowering its reactivity. This results in sequential reactivity useful for controlled polymerization. In contrast, 2,6-TDI presents greater steric shielding for both isocyanates, contributing to slower overall reactivity (Table 1) [13, 17].

MDI exists primarily as 4,4′-MDI, although 2,4′- and 2,2′-isomers also occur. Polymeric MDI (pMDI) represents a mixture of higher oligomeric species, conferring functionality beyond two isocyanate groups per molecule. The rigidity of the diphenylmethane backbone, coupled with conjugation between the aromatic ring and the –NCO groups, stabilizes the electrophilic carbon of the isocyanate, while favoring linear hard-segment formation in polymers [18].

2.2. Electronic effects on reactivity of the –N=C=O group

The isocyanate functional group exhibits a polarized structure: the carbon of the –N=C=O moiety is strongly electrophilic, activated by resonance and inductive effects of the adjacent nitrogen and oxygen atoms. In aromatic isocyanates, conjugation with the ring further stabilizes the group but enhances reactivity toward nucleophiles due to electron-withdrawing effects (Figure 2).

Table 1. Comparison of the structural characteristics, physical properties, reactivity, and typical application domains of MDI and TDI

Property	MDI	TDI
Molecular structure	Symmetrical aromatic diisocyanate with diphenyl core	Asymmetrical toluene ring with ortho-/para-isomers (2,4- and 2,6-TDI)
Reactivity	More controlled, slower than TDI	Faster reactivity, more flexible formulations
Physical form	Solid (flakes/prills) at RT	Liquid at RT
Typical applications	Rigid foams, CASE, composites	Flexible foams, elastomers
Advantages	High mechanical strength, thermal stability	Cost-effective, high reactivity, flexibility
Limitations	Processing requires melting/solvent, higher cost	Higher toxicity, less thermal stability

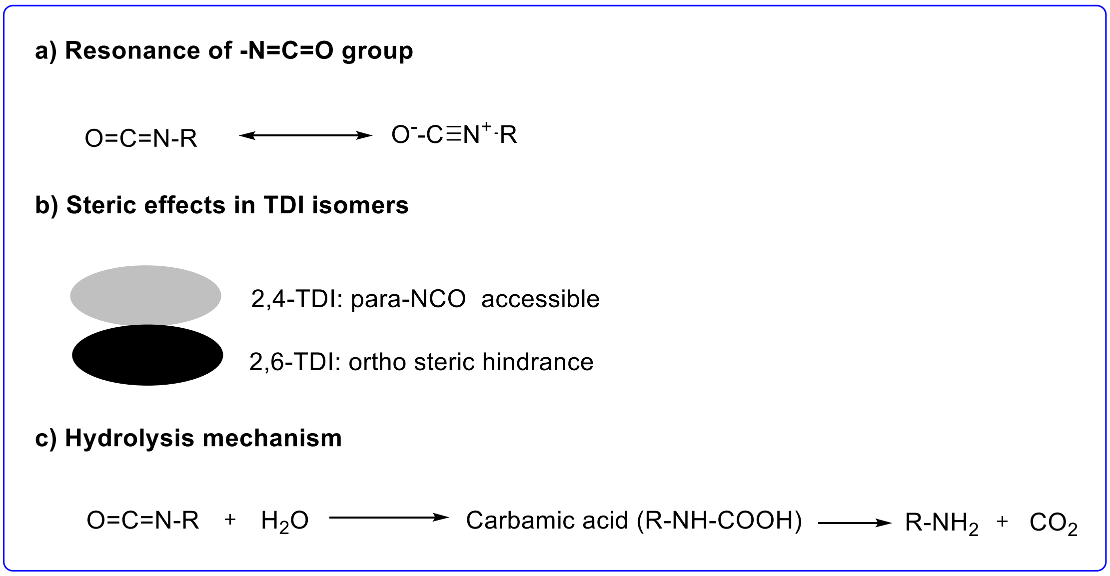

Fig. 2. Structural features and electronic reactivity of aromatic diisocyanates

Nucleophilic addition to the isocyanate carbon is the basis of urethane formation. Alcohols attack to form carbamate linkages, while amines generate substituted ureas. Reaction with water produces unstable carbamic acid intermediates that decarboxylate to amines, releasing CO_2 — a mechanism crucial in foam formation. The relative reactivity of isomers reflects steric accessibility and electronic influences: 2,4-TDI reacts faster than 2,6-TDI, while 4,4′-MDI demonstrates balanced reactivity suited to both elastomers and foams [19-22].

2.3. Polyurethane synthesis routes

From a synthetic perspective, several approaches are employed:

Bulk polymerization: Direct addition of isocyanates to polyols without solvents. Thermally efficient but requires strict control of exothermicity [23, 24].

Solution polymerization: Conducted in inert organic solvents, improving control over viscosity and chain extension. Particularly valuable for coatings and adhesives [18, 25].

Emulsion polymerization: Formation of waterborne PU dispersions (PUDs) through prepolymer emulsification, offering low-VOC alternatives with significant industrial uptake [25, 26].

Reaction injection molding (RIM): A rapid, high-pressure process relying on the fast kinetics of isocyanate addition, producing shaped articles with excellent dimensional stability [27, 28].

In solution, polar aprotic solvents can stabilize the transition state of the isocyanate–alcohol addition, thereby accelerating urethane bond formation, whereas less polar media often reduce the effective reaction rate and favor side reactions such as isocyanate trimerization. Catalysts, ranging from tertiary amines to organometallic species (e.g., dibutyltin dilaurate), further tune reactivity by either enhancing nucleophilicity of the polyol or increasing the electrophilicity of the –NCO carbon. Mechanistic studies have shown that the choice of catalyst not only impacts reaction rate but also the distribution of urethane versus allophanate and biuret linkages, which in turn affects the mechanical and thermal properties of the resulting polymer (Table 2).

The isomeric structure of the diisocyanate plays a decisive role as well: in 2,4-TDI the para-isocyanate group is significantly more reactive than the ortho-substituted one, while in MDI the symmetry and electronic distribution of the phenyl rings produce different reactivity patterns between the 4,4′-, 2,4′-, and 2,2′-isomers.

These subtle differences in regiochemistry and electronic effects directly translate into variations in molecular weight distribution, crosslink density, and ultimately, the macroscopic performance of polyurethane materials [29, 30].

2.4. Catalysts and organocatalysts: Mechanistic role

Catalysts dramatically influence both rate and selectivity of isocyanate reactions.

Tertiary amines (e.g., triethylene diamine) accelerate urethane formation and CO_2 generation, while organotin catalysts (e.g., dibutyltin dilaurate) enhance carbamate linkage formation with high efficiency (Figure 3 and 4) [31-34]. Recent trends emphasize environmentally benign alternatives: bismuth and zinc salts, ionic liquids, and organocatalysts such as *N*-heterocyclic carbenes. Mechanistically, these catalysts lower activation barriers by stabilizing transition states or activating nucleophiles, thereby altering the competitive balance between urethane, urea, and side-product formation [35, 36].

Table 2. Common catalytic systems and competing reaction pathways in MDI- and TDI-based polyurethane formation, with their structural and property implications.

Transformation	Catalyst(s)	Effect on PU Structure
Urethane formation	Tertiary amines, organotin, bismuth/zinc catalysts	Promotes NCO–OH reaction (main pathway)
Allophanate	Organotin, Zn, Bi	Creates crosslinks, increases hardness
Biuret	Organotin, high-temp conditions	Adds branching, improves thermal stability
Carbodiimide	Phospholine oxide, carbodiimide-forming catalysts	Improves heat resistance, reduces free NCO
Uretdione	Organophosphorus catalysts	Latent curing, storage stability

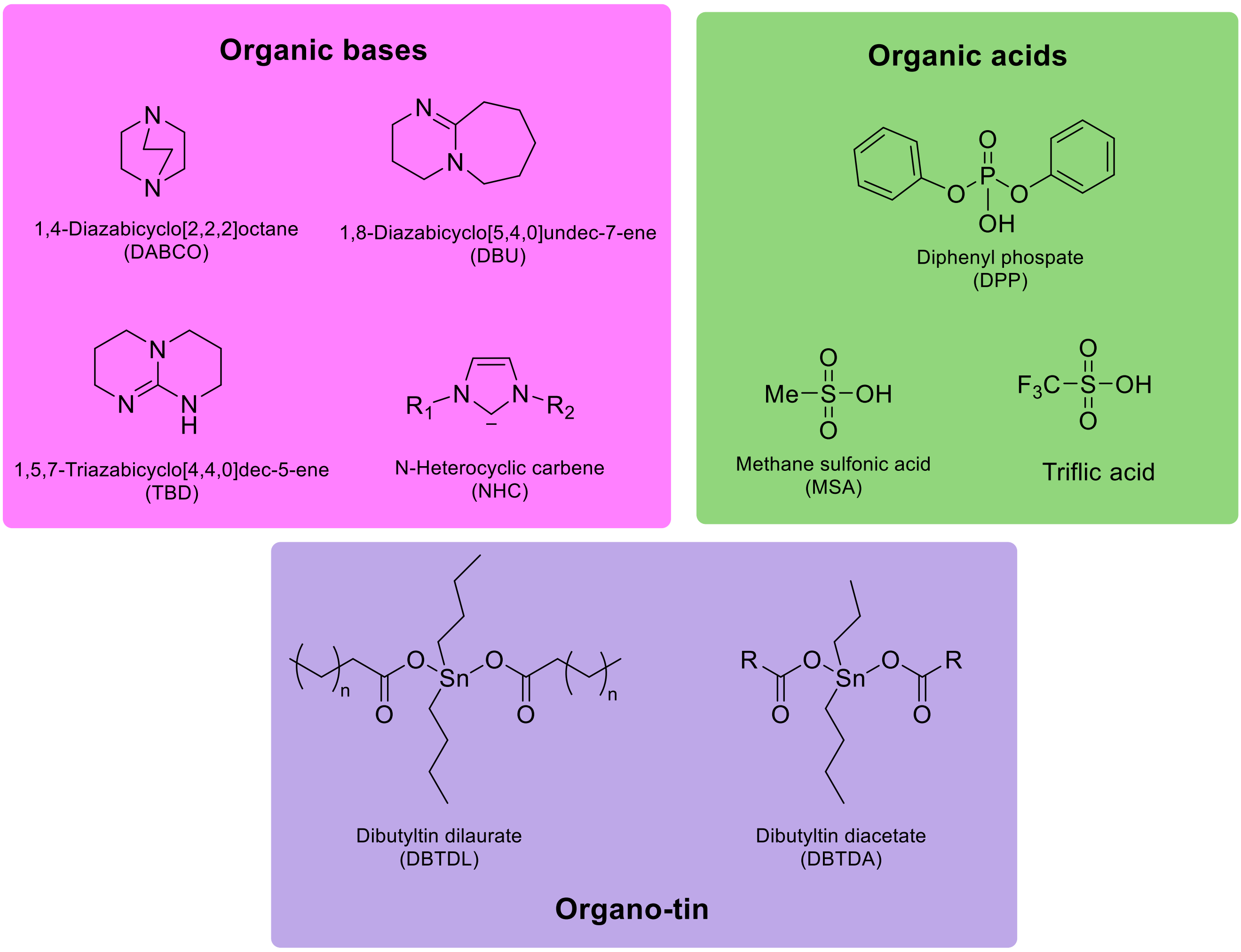

Fig. 3. Conventional organic acids, bases and tin catalysts employed in the isocyanate-based PU synthesis [31]

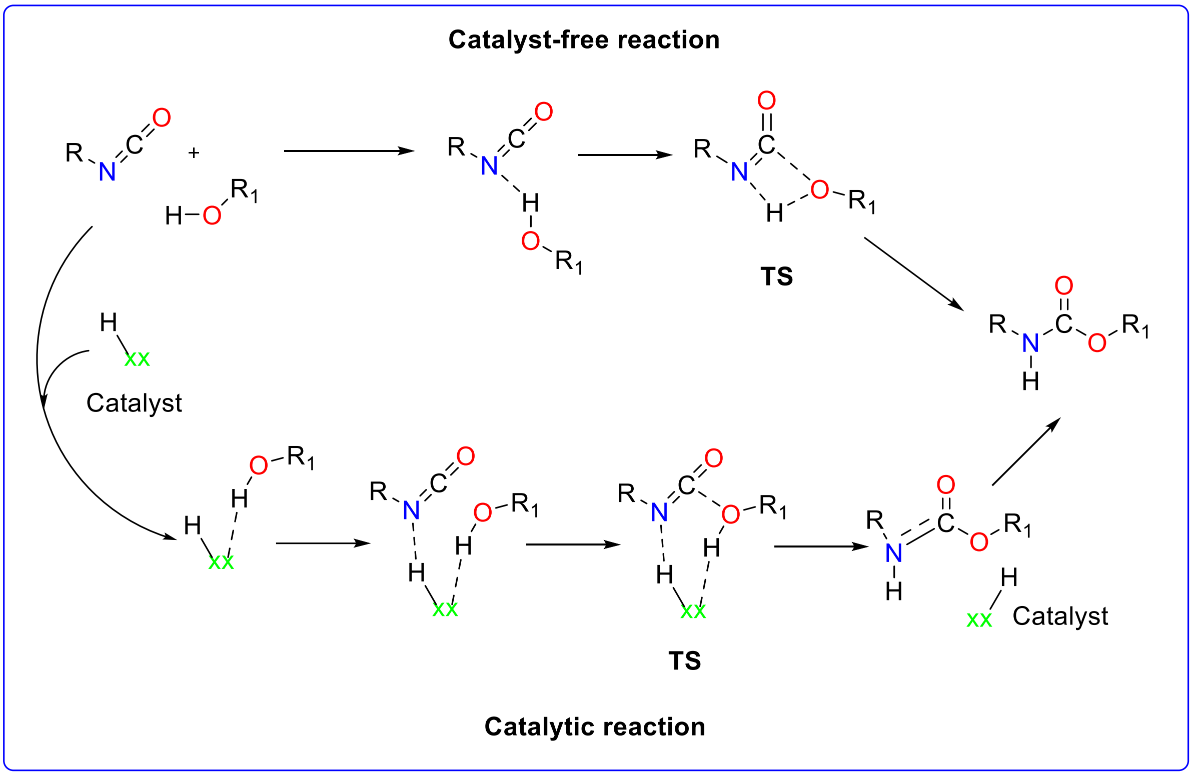

Fig. 4. Schematic illustration of the general reaction pathway between isocyanates and alcohols, shown without catalysts (top) and with acid catalysts (bottom) [34].

2.5. Side reactions and competing organic transformations

Isocyanates engage in several secondary organic reactions that profoundly affect polymer microstructure:

Allophanate formation: Reaction of urethanes with excess isocyanates, producing crosslinked structures [37].

Biuret formation: Urea linkages reacting further with isocyanates, enhancing rigidity.

Carbodiimide and uretdione formation: Thermal or catalytic dimerization of isocyanates, important in storage stability and prepolymer modification.

Hydrolysis and oxidative degradation: Pathways leading to amines, CO_2, and oligomeric fragments.

These competing reactions highlight the organic complexity of PU synthesis, where even subtle changes in reaction conditions can significantly impact the final architecture and performance [38, 39, 2].

3. Structure–property relationships from a molecular perspective

3.1. Microphase separation and segmented morphology

PUs are inherently segmented copolymers. The polarity of hard segments (diisocyanate + chain extender) contrasts with the nonpolar nature of soft segments (polyol chains), promoting microphase separation. Hydrogen-bonded hard domains aggregate into physically crosslinked regions that reinforce the softer matrix. MDI-based systems exhibit stronger phase separation due to their linear rigid structure, whereas TDI yields more amorphous morphologies (Table 3) [40-43].

Table 3. Key structure–property relationships in MDI- and TDI-based polyurethanes, highlighting the influence of molecular features on mechanical, thermal, and chemical performance.

Structural Feature	Impact on Properties
High hard segment content	Increase modulus, Increase hardness, Decrease flexibility
Soft segment (polyol type, MW)	Controls elasticity, flexibility, Tg
Hydrogen bonding density	Increase phase separation, Increase mechanical strength
Aromatic content (MDI/TDI)	Increase thermal stability, Increase stiffness
Crosslink density	Increase dimensional stability, Decrease elongation

3.2. Intermolecular interactions

Hard and soft segment interactions are mediated by hydrogen bonding, π–π stacking among aromatic rings, and van der Waals forces. The density and strength of these interactions directly influence modulus, resilience, and thermal stability.

MDI's symmetric structure promotes more ordered packing, while TDI's isomeric asymmetry leads to reduced order but greater flexibility [44, 45].

3.3. Thermal properties

Thermal transitions reflect the dual-segment nature of PUs [46-49]:

Glass transition temperature (Tg): Governed by polyol chemistry; polyether PUs show low Tg, while polyester-based systems are higher.

Melting transitions (Tm): Associated with crystalline ordering of hard segments, more prominent in MDI-based systems.

Thermal degradation: Typically occurs in two stages: urethane/urea breakdown (200–350 °C), followed by polyol decomposition (>350 °C). MDI-derived PUs show enhanced stability.

3.4. Mechanical properties

Mechanical strength correlates with chemical composition:

High hard segment content → increased tensile strength and modulus.

Low hard segment content → improved elongation and elasticity.

MDI-based elastomers achieve Shore hardness and abrasion resistance suitable for industrial wheels, while TDI-based elastomers excel in resilience and cushioning [50-54].

3.5. Chemical and environmental resistance

Chemical durability is shaped by molecular design: ***Hydrolytic stability:*** Greater for MDI-based PUs, especially with polycarbonate polyols.

Solvent resistance: Higher crosslinking and aromaticity improve solvent tolerance.

Photodegradation: Aromatic diisocyanates are susceptible to UV-induced yellowing, requiring stabilizers. These degradation pathways parallel classical hydrolysis, oxidation, and photolysis mechanisms studied in small molecules, yet manifest here in the context of complex polymeric networks (Figure 5) [55-57].

4. Applications of MDI and TDI-based polyurethanes

The application domains of MDI- and TDI-based polyurethanes differ significantly due to their inherent structural and reactivity profiles. As summarized in Table 4, MDI is predominantly employed in rigid foams, composites, and CASE applications, whereas TDI is favored in flexible foam formulations.

4.1. Rigid foams

Rigid foams, predominantly MDI-based, exploit high crosslink density to create closed-cell structures with excellent compressive strength and thermal insulation. Their performance stems from chemical crosslinking reactions (allophanate, biuret formation) that produce a stable three-dimensional network. Applications include building insulation panels, cold storage, and appliance linings [58-60].

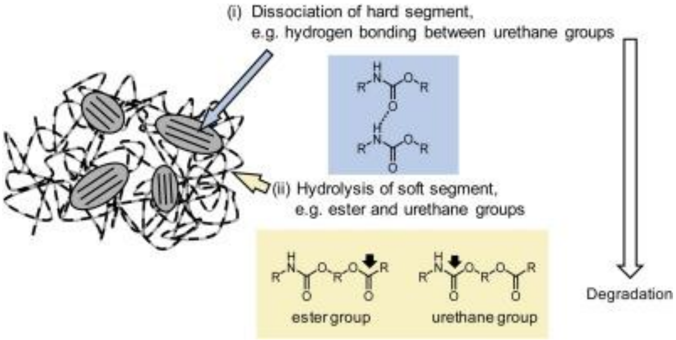

Fig. 5. Solvent-induced degradation of polyurethane [55]

Table 4. Major application areas of polyurethanes derived from MDI and TDI

Application Area	Predominant Diisocyanate	Key Properties
Rigid foams	MDI	Thermal insulation, compressive strength
Flexible foams	TDI	Cushioning, resilience
CASE (Coatings, Adhesives, Sealants, Elastomers)	Both (MDI-rich systems for performance)	Durability, adhesion, chemical resistance
Composites	MDI	Strong interfacial bonding, mechanical reinforcement
Biomedical PUs	MDI (purified grades)	Biocompatibility, tunable degradation

4.2. Flexible foams

Flexible foams, mainly based on TDI, capitalize on fast reactivity and controlled phase separation to produce open-cell structures. The sequential reactivity of 2,4- and 2,6-isocyanate groups enables fine-tuned curing, yielding materials with high resilience, cushioning, and elongation. These are indispensable in mattresses, furniture, and automotive seating [49].

4.3. Coatings, adhesives, sealants, and elastomers (CASE)

Both MDI and TDI derivatives are widely applied in CASE sectors:

Coatings: Urethane linkages provide chemical resistance and toughness; MDI-based systems offer superior durability.

Adhesives: MDI prepolymers bond strongly to diverse substrates, benefiting from multiple reactive sites.

Sealants: MDI-based sealants resist hydrolysis and environmental degradation.

Elastomers: MDI yields high-hardness elastomers, while TDI produces flexible, resilient formulations [24].

4.4. Composites and hybrid systems: interfacial bonding mechanisms

Polyurethanes (PUs) are increasingly integrated into composite and hybrid systems to combine the intrinsic versatility of the urethane network with the structural or functional advantages of reinforcing agents. The success of these systems depends heavily on the interfacial bonding mechanisms, which are dictated by the chemistry of MDI and TDI.

Fiber-reinforced PU composites: Glass and carbon fibers, widely used in structural composites, present hydroxylated or oxidized surfaces that react with the –NCO groups of MDI or TDI. Covalent bonding at the fiber–matrix interface improves stress transfer efficiency, enhancing tensile strength and impact resistance [61, 62]. MDI-based systems, with higher functionality and stronger hydrogen bonding, often yield composites with superior load-bearing capacity compared to TDI-based systems.

Nanocomposites: Incorporation of nanofillers such as graphene oxide, cellulose nanocrystals, silica nanoparticles, and layered silicates exploits interfacial chemistry [63, 64]. For example, graphene oxide contains hydroxyl, carboxyl, and epoxy groups that can react with isocyanates, forming covalent urethane or urea bonds. Such reactions improve dispersion and interfacial adhesion, translating to improved thermal stability, flame retardancy, and electrical conductivity.

Hybrid polymer systems: PU–epoxy hybrids are notable for combining the flexibility of urethanes with the rigidity of epoxy crosslinks. Chemical compatibility is achieved by isocyanate groups reacting with hydroxyl or amine functionalities of the epoxy curing agents, producing an interpenetrating polymer network (IPN). Similarly, PU–polyurea hybrids leverage the nucleophilic reactivity of diamines, yielding materials with enhanced toughness and chemical resistance [65,66].

Thus, the central theme is the reactivity of the isocyanate group toward nucleophilic functionalities on reinforcements or copolymers. This reactivity governs not only interfacial adhesion but also phase morphology and, ultimately, composite performance.

4.5. Biomedical and healthcare applications: structure–biocompatibility correlation

Polyurethanes have long been attractive in the biomedical field due to their unique combination of mechanical flexibility, biocompatibility, and chemical tunability. The role of MDI and TDI chemistry is particularly important in dictating the relationship between chemical structure and biological performance.

MDI-based biomedical PUs: MDI is preferred over TDI for biomedical applications because of its lower volatility, greater hydrolytic stability, and reduced leaching of aromatic degradation products. The rigid aromatic backbone of 4,4′-MDI provides dimensional stability, while careful design of soft segments (polyether, polyester, or polycarbonate polyols) allows adjustment of elasticity and compliance to match biological tissues. For example, polycarbonate-based PUs are especially valued in long-term implants due to resistance to hydrolytic degradation [67, 68].

TDI-based biomedical PUs: Historically, TDI-based foams and elastomers were used in wound dressings, surgical pads, and medical tubing. However, the relatively higher volatility of TDI, combined with its tendency to undergo oxidative degradation and discoloration, has limited its adoption in implantable devices. Nevertheless, TDI foams are still used in short-term biomedical cushioning and disposable medical products [68, 69]. Structure–biocompatibility correlations: Biocompatibility depends strongly on the chemical structure. Factors such as the density of hard segments, degree of hydrogen bonding, and presence of residual unreacted isocyanates influence protein adsorption, cellular adhesion, and inflammatory response. Aromatic PUs, while mechanically robust, can be prone to oxidative degradation in vivo, leading to aromatic diamine release. Modifications such as surface coatings, blending with aliphatic diisocyanates, or incorporating biostable polyols are strategies to improve hemocompatibility and long-term stability.

Emerging biomedical PU systems: Advances include PU hydrogels for tissue scaffolds, drug-eluting PU coatings for stents, and stimuli-responsive PU carriers for controlled drug release. In many cases, the presence of aromatic isocyanate-derived hard segments offers mechanical reinforcement, while the organic chemistry of soft segments governs biodegradation rates and tissue compatibility.

Thus, for biomedical applications, the challenge lies in balancing organic structural design (choice of diisocyanate, polyol, and chain extender) with the stringent requirements of biostability and biocompatibility.

5. Challenges and limitations

Despite their extensive industrial utility, MDI- and TDI-based polyurethanes face several fundamental challenges. These challenges relate to the inherent chemical nature of aromatic isocyanates, their environmental footprint, and the complexities of end-of-life management.

5.1. Toxicity and occupational exposure of aromatic isocyanates

Aromatic diisocyanates such as MDI and TDI are classified as potent respiratory sensitizers and are subject to stringent occupational safety regulations. The toxicity arises from the high electrophilicity of the –N=C=O functional group, which readily reacts with nucleophilic sites on biomolecules (e.g., amine, thiol, hydroxyl groups of proteins).

TDI: Due to its higher volatility and vapor pressure, TDI poses a greater inhalation hazard. Workers in foam production facilities are particularly at risk. Even short-term exposure can cause asthma, rhinitis, and long-term respiratory sensitization.

MDI: While less volatile than TDI, MDI still presents hazards during the handling of monomers and prepolymers. Aerosolized particles (e.g., from spray foams) present inhalation and dermal risks.

From an organic chemistry viewpoint, the reactivity of isocyanates with nucleophilic biomolecules is mechanistically analogous to their polymerization chemistry: electrophilic carbonyl-type addition reactions that form covalent adducts. This explains the irreversible sensitization effect — once covalent adducts are formed with proteins, the immune system is triggered.

Thus, occupational handling requires engineering controls (ventilation, closed systems), PPE, and regulatory monitoring (e.g., OSHA, REACH). Toxicity remains one of the strongest limitations on expanding isocyanate use, particularly in consumer-facing products.

5.2. 5.2 Environmental persistence and sustainability concerns

Polyurethanes derived from MDI and TDI are highly durable materials, which contributes to their industrial success but also raises issues of environmental persistence. Crosslinked PU foams are essentially thermoset plastics with limited degradability.

Persistence in the environment: The aromatic structure of MDI and TDI hard segments contributes to high resistance against hydrolysis, microbial degradation, and UV breakdown. In particular, aromatic PUs fragment slowly under environmental conditions, producing microplastic-like particles [70].

Degradation pathways: Hydrolytic cleavage of urethane bonds can produce aromatic diamines (e.g., toluene diamine from TDI degradation, methylenedianiline from MDI), which are themselves toxic and potentially carcinogenic.

Sustainability of feedstocks: Both MDI and TDI are produced from petrochemical feedstocks (e.g., aniline and formaldehyde for MDI; toluene and phosgene for TDI). This reliance on fossil resources, along with the use of phosgene, highlights sustainability and safety issues in upstream production [71].

These issues motivate efforts toward bio-based polyols**,** alternative isocyanates (from non-phosgene routes), and even non-isocyanate polyurethane (NIPU) chemistries. However, balancing sustainability with performance remains a challenge.

5.3. Recycling barriers: mechanistic considerations in chemical vs. mechanical recycling

End-of-life management of PU materials, especially foams, presents one of the largest challenges for the industry.

Mechanical recycling: Grinding PU waste into powder for use as fillers in new formulations is straightforward but limited. Crosslinked PUs cannot be remelted or reprocessed due to their network structure. The resulting recycled material often shows inferior properties, restricting applications.

Chemical recycling: Organic chemists have explored **glycolysis,** hydrolysis, aminolysis, and alcoholysis to break urethane linkages and recover polyols. Mechanistically, these processes involve nucleophilic attack at the urethane carbonyl, cleaving the C–O bond and generating diols plus amines.

Glycolysis (attack by ethylene glycol, diethylene glycol) is the most industrially relevant, but it produces complex mixtures of polyols requiring purification [72]. Hydrolysis at elevated temperatures can yield diamines, but controlling byproducts is difficult [73, 74].

Dynamic covalent chemistry: Recent research has introduced exchange reactions (urethane–urethane exchange, transcarbamoylation) to design reprocessable PUs (vitrimers)**.** Mechanistically, these rely on reversible bond exchange reactions that allow reshaping without full depolymerization [75].

The challenge lies in scalability: while laboratory methods demonstrate feasibility, industrial-scale chemical recycling of MDI/TDI PUs remains energy-intensive and costly.

5.4. Balancing performance and cost in structure–property optimization

One of the enduring limitations of MDI- and TDI-based systems is the tension between performance requirements and economic feasibility**.**

Performance drivers: High-performance formulations often require higher hard segment content, specialty polyols (e.g., polycarbonate diols), nanofillers, or catalysts that add significant cost. Biomedical-grade PUs demand strict purification and biocompatibility testing, further raising expenses.

Cost drivers: TDI remains cheaper and easier to process than MDI, which explains its dominance in flexible foam production. However, MDI provides superior properties for rigid foams and elastomers. Switching to bio-based polyols or greener catalysts can increase raw material costs.

Trade-offs: Manufacturers often balance cost and performance by using blends (e.g., TDI/MDI mixtures in foams) or hybrid systems. This can achieve adequate mechanical properties at reduced cost but may compromise durability or recyclability.

From a structure–property perspective, the challenge is to **rationally design PU formulations** that optimize molecular interactions (hydrogen bonding, crosslink density) while controlling raw material costs and minimizing environmental and health impacts.

6. Recent advances in MDI and TDI-based polyurethanes

Recent research has focused not only on performance optimization but also on the sustainability and recyclability of MDI- and TDI-based polyurethanes. Table 5 summarizes key advances, ranging from bio-based polyols and greener synthetic routes to self-healing systems, nanocomposites, and biomedical applications.

6.1. Bio-based polyols and greener synthetic strategies

Replacing petroleum polyols with bio-derived polyols reduces cradle-to-gate carbon intensity and creates new chemical functionality for PU design (Figure 6). The goal is a drop-in or near-drop-in substitution that preserves performance while improving sustainability.

Major classes of bio-based polyols: **Vegetable-oil derived polyols** (epoxidation + ring-opening of fatty esters; hydroxylated vegetable oils such as epoxidized soybean oil → glycidyl esters → polyols). These provide flexibility and hydrophobicity; useful in flexible foams and coatings [12, 71].

Lignin-derived polyols (chemical modification of lignin phenolic units to afford polyol functionality). High aromatic content increases hardness and UV/thermal stability but requires depolymerization/modification to reduce polydispersity [76-79].

Sugar- and carbohydrate-based polyols (e.g., sorbitol, xylitol derivatives) provide multiple hydroxyl sites enabling highly crosslinked networks [11].

Bio-polyesters / polycarbonates produced from lactones or CO_2 fixation (e.g., poly(trimethylene carbonate) diol from 1,3-propanediol) combine hydrolytic stability and tuneable Tg [11].

Synthetic strategies & organic chemistry challenges

a) Functionalization chemistry: Converting biopolymers into polyols requires selective functional group transformations: epoxidation (alkene → epoxide), controlled ring opening (epoxide → vicinal diol), esterification/transesterification, and hydroxyalkylation. Regio- and stereocontrol influence polyol properties (backbone flexibility, OH accessibility) [80, 81].

b) Control of OH functionality and molecular weight: For predictable hard/soft segment architecture, functionality (favg) and Mn distribution must be controlled. Synthetic routes (controlled ring-opening polymerizations, catalytic depolymerization of lignin) are active research areas [82].

c) Compatibility & phase behavior: Bio-polyols often bring polar groups or bulky aromatics (lignin) that change microphase separation with MDI/TDI. Compatibilization strategies include end-group capping, grafting, or using copolymer polyols [76, 81].

Table 5. Emerging advances and research trends in MDI- and TDI-based polyurethane systems, including sustainable feedstocks, functional modifications, nanocomposites, recycling strategies, and biomedical developments

Area	Representative Strategy	Key Outcomes
Bio-based polyols	Vegetable oils, lignin, glycerol derivatives	Reduced fossil dependence, comparable properties
Greener isocyanate routes	Non-phosgene, CO_2-based	Lower toxicity, sustainable production
Self-healing PUs	Urethane exchange, disulfide bonds, Diels–Alder	Extended lifetime, reprocessability
Nanocomposites	Graphene, nanoclays, CNTs	↑ Mechanical, barrier, flame resistance
Recycling	Glycolysis, transcarbamoylation, hydrolysis	Circular economy pathways
Biomedical PUs	Polycarbonate diols, MDI-based TPUs	Improved biocompatibility, hemocompatibility

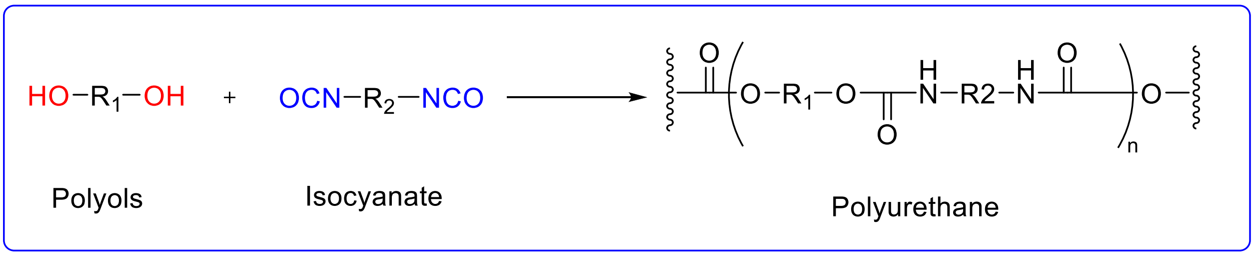

Figure 6. Synthetic route of polyurethane from diisocyanates and polyols

d) Green isocyanate routes**:** Addressing phosgene use (in industrial isocyanate production) has led to non-phosgene routes (e.g., oxidative carbonylation, Curtius rearrangement variants, urea → isocyanate via decomposition) and research into biomass-derived isocyanates, though scalable alternatives remain limited [83].

Performance tradeoffs & examples

a) Vegetable-oil polyols: good flexibility but lower mechanical strength and oxidation susceptibility - often copolymerized with petroleum polyols or reinforced with fillers.

b) Lignin polyols: improved rigidity and thermal stability; require fractionation and controlled depolymerization to reduce heterogeneity [12, 84].

6.2. Functional modifications: Self-healing, shape-memory, flame-retardancy

Dynamic covalent chemistries embedded in PU backbones allow bond exchange and healing:

Transcarbamoylation / urethane exchange: reversible exchange between urethane linkages (typically thermo-activated or catalyzed by organocatalysts/metal salts). Reaction: R–O–(C=O)–NH–R' ⇌ R–O–(C=O)–NH–R'' (exchange). The key is balancing the exchange rate (reprocessability) versus service stability [85-87].

Disulfide exchange**:** S–S bonds introduced in chain extenders permit redox or thermally driven healing.

Imine (Schiff base) bonds, boronic ester, Diels–Alder adducts**:** reversible linkages for stimulus-responsive healing. ***Vitrimers*****:** covalent networks with associative exchange reactions (no change in crosslink density) that allow flow at elevated temperature while retaining crosslinked integrity at service temps. PU vitrimers have employed urethane exchange or transcarbamoylation catalyzed by Zn/Bi salts or organic bases.

Design principle: a two-phase system where hard segments serve as fixed points and soft segments (with Tg/Tm in the programming range) store temporary shapes. MDI hard blocks provide robust switching segments; choice of polyol (polyether vs polyester) tunes switching temperature.

Molecular levers: control hydrogen bonding density, crystallinity of soft blocks, and crosslink density to tune actuation temperature, recovery stress, and cycling stability.

Reactive flame retardants vs additive approaches: Reactive phosphorus-containing polyols (phosphonate or phosphate end-groups) chemically introduce flame retardancy while minimizing migration. Halogen-free intumescent systems (polyphosphate-based) combined with expandable graphite or nano-fillers.

Role of aromatic hard domains**:** MDI-rich PUs generally char better (aromatic content) than aliphatic analogs; combining with phosphorus increases char formation and reduces heat release.

Incorporating dynamic bonds can reduce thermal/mechanical stability or alter Tg; catalysts required for exchange may affect long-term stability and biocompatibility. Flame retardants can plasticize or catalyze degradation; choosing covalently bound (reactive) FRs reduces leaching and regulatory concerns.

6.3. Nanocomposites and filler-reinforced PU systems

Nanofillers at low loadings dramatically alter modulus, thermal stability, barrier properties, flame retardancy, and conductivity by reinforcing the matrix and creating tortuous paths for diffusion [88-90].

Graphene/graphene oxide (GO): GO carries –OH, –COOH, epoxy groups that can react with –NCO to form covalent linkages (urethane/urea), improving dispersion and interfacial adhesion.

Carbon nanotubes (CNTs): surface functionalization (carboxylation, grafted polyols) is critical to avoid bundles and enhance load transfer; covalent bonding to matrix via –NCO reactions or noncovalent wrapping with compatibilizers is used.

Layered silicates / nanoclays: organomodified clays intercalate with polyols; exfoliation achieved via in situ polymerization or solvent processing.

Cellulose nanocrystals (CNCs) / nanofibrillated cellulose: abundant hydroxyl groups react with –NCO or can be surface-modified (silylation, grafting) to improve dispersibility; gives biodegradability and mechanical reinforcement.

Silica nanoparticles: usually functionalized with alkoxy silanes bearing hydroxyls or amine groups to react with isocyanates or act as compatibilizers.

Surface functionalization / grafting: grafting polyol chains or reactive groups onto filler surfaces ensures covalent/strong interfacial bonding (reaction of surface –OH/–NH_2 with –NCO).

In situ polymerization / prepolymer approaches: disperse functionalized filler in polyol or prepolymer before chain extension to ensure exfoliation and bonding.

Use of compatibilizers: block copolymers, surfactants, or reactive diluents promote dispersion and prevent aggregation.

Mechanical reinforcement: load transfer occurs via covalent or strong interfacial bonds; filler aspect ratio and dispersion govern modulus gains.

Thermal and flame performance: barrier effects, char promotion, and catalytic char formation (with certain fillers) reduce heat release and slow degradation.

Electrical/thermal conductivity: percolation of conductive fillers (CNTs/graphene) gives antistatic, EMI shielding, or thermal conduction properties useful in electronics or thermal management. *Challenges:* Achieving uniform dispersion at scale without degrading isocyanate reactivity. Preserving PU processability (viscosity control) when adding high-aspect fillers. Ensuring long-term interfacial stability (hydrolysis, oxidative environments).

6.4. Circular economy approaches and chemical recycling pathways

Circular strategies aim to recover monomers/oligomers or enable reuse of polymeric networks. Approaches fall into mechanical recycling**,** chemical recycling (depolymerization / solvolysis)**,** and design for recyclability (vitrimers, dynamic networks) [72, 74, 91-93]**.**

6.4.1. Chemical recycling routes (mechanistic perspective)

Glycolysis (transesterification-like): polyol or glycol nucleophile attacks urethane carbonyl, cleaving the C–O bond and producing oligomeric/polyol fragments. Typical nucleophiles: ethylene glycol, diethylene glycol. Mechanism: nucleophilic acyl substitution via tetrahedral intermediate. Product complexity requires distillation/purification for reuse.

Hydrolysis: water (often under acidic/basic catalysis) cleaves urethane to give amines and polyols — typically less selective and requires severe conditions.

Aminolysis: amines attack urethane carbonyl giving urea formation and polyol fragments; used to recover useful intermediates but generates amine-rich waste streams.

Solvolysis & alcoholysis: use alcohols to depolymerize, similar to glycolysis.

Pyrolysis: thermal cracking yields small molecules (aromatics, amines) but lacks selectivity and requires downstream upgrading.

6.4.2. Design for chemical recycling

End-of-life labeling / controlled linkages: incorporating cleavable linkers (e.g., ester, disulfide) at specific positions enables targeted depolymerization under mild conditions. ***Vitrimers / dynamic covalent networks:*** enable reshaping and repair; when combined with depolymerization routes, enable hybrid circularity (reprocess + chemical recovery). ***Catalyst development:*** selective, mild catalysts (organocatalysts, enzyme mimics) for targeted depolymerization could lower energy and purification costs.

6.4.3. Practical & economic barriers

Feedstock heterogeneity: PU waste streams are mixed; sorting is required.

Energy & solvent demands: many chemical recycling processes require heat/solvents and produce mixed byproducts.

Purity of recovered materials: glycolysates often require re-refinement before repolymerization to high-performance PUs. ***Regulatory & collection infrastructure:*** closed-loop relies on collection systems and incentives.

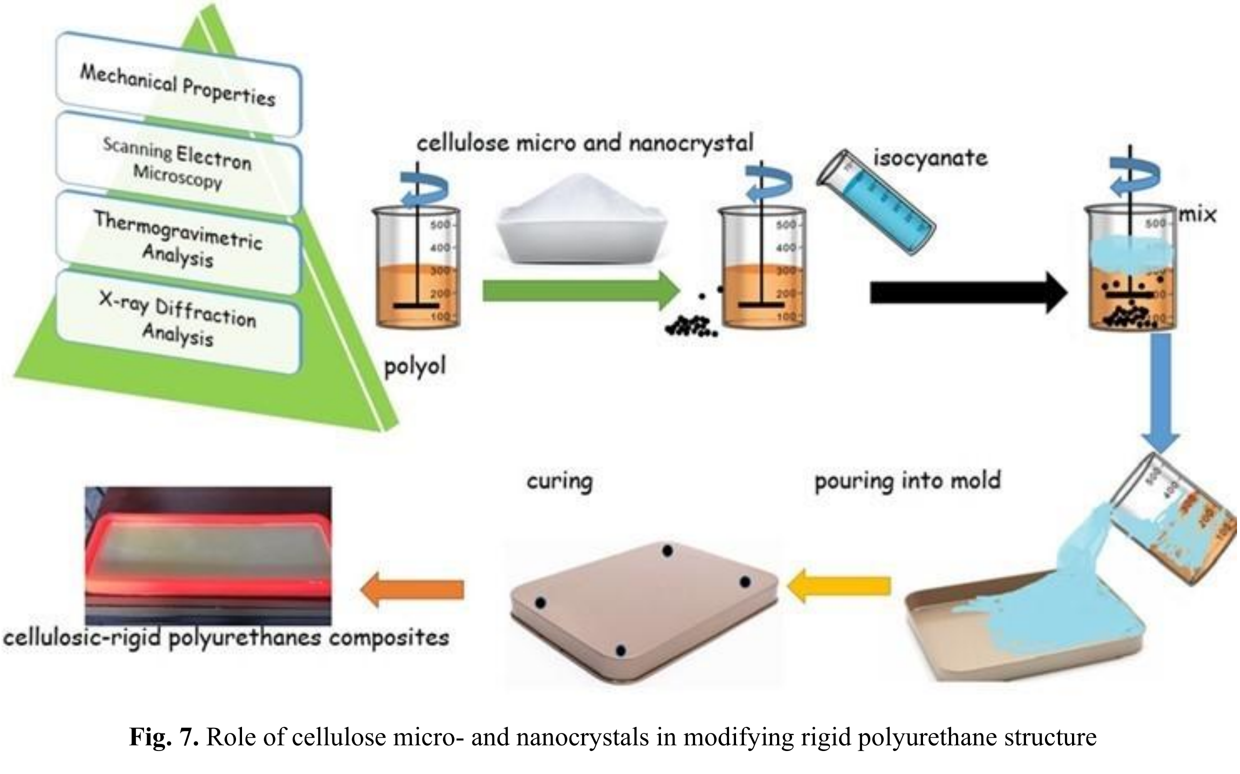

Fig. 7. Role of cellulose micro- and nanocrystals in modifying rigid polyurethane structure

6.5. Biocompatible and biomedical PU materials

6.5.1. Design criteria for biomedical PUs

Biomedical applications (implants, devices, drug delivery) require control over biostability, degradation profile, cytotoxicity, and surface interactions (protein adsorption, cell adhesion) [94-99]. A representative preparation of polyether urethane (Pellethane®) is depicted in Figure 8.

6.5.2. Structural strategies

Choice of diisocyanate: aliphatic diisocyanates are generally favored for long-term implants due to UV stability and lower aromatic degradation products; however, MDI can be used when mechanical demands are high and well-engineered purification/surface treatment minimize leachable species.

Soft segment selection: polycarbonate diols provide superior hydrolytic stability; polyether diols (PEG-type) reduce protein adsorption and improve hemocompatibility.

End-group blocking & purification: blocking residual –NCO and exhaustive post-curing reduce leachable isocyanates and aromatic diamines.

Surface modification: PEGylation, zwitterionic coatings, or immobilized bioactive peptides reduce fouling and tailor cellular responses.

6.5.3. Degradation & biocompatibility mechanisms

Hydrolytic backbone scission (ester linkages in polyester polyols) leads to controlled degradation; aromatic urethane backbones are more persistent. Oxidative degradation by reactive oxygen species in vivo can lead to chain scission, particularly at soft-segment ether linkages.

Leachables: aromatic diamines from degradation are toxic; minimizing their generation (via aliphatic alternatives or protective chemistries) is crucial [101-103].

6.5.4. Applications & examples

Cardiovascular devices: polyurethane coatings on stents or catheters requiring hemocompatibility and flexibility.

Tissue engineering scaffolds: biodegradable PU elastomers tuned for modulus and degradation matched to target tissue.

Drug delivery: PU nanoparticles or hydrogels designed for controlled release; stimuli-responsive linkers (pH, enzyme-cleavable) enable targeted delivery [104].

6.5.5. Sterilization and regulatory considerations

Sterilization (autoclave, gamma, EtO) can affect PU chemistry (crosslinking, chain scission); formulation must tolerate chosen sterilization. Regulatory pathways (ISO standards, biocompatibility testing) require extensive chemical characterization (residuals, extractables) and long-term stability data.

7. Future perspectives

Advancing MDI- and TDI-based polyurethanes toward safer, greener, higher-function materials will require coordinated progress in small-molecule organic chemistry, catalysis, polymer reaction engineering, and materials science.

The subsections below identify promising directions where mechanistic understanding and molecular design can deliver step-change improvements.

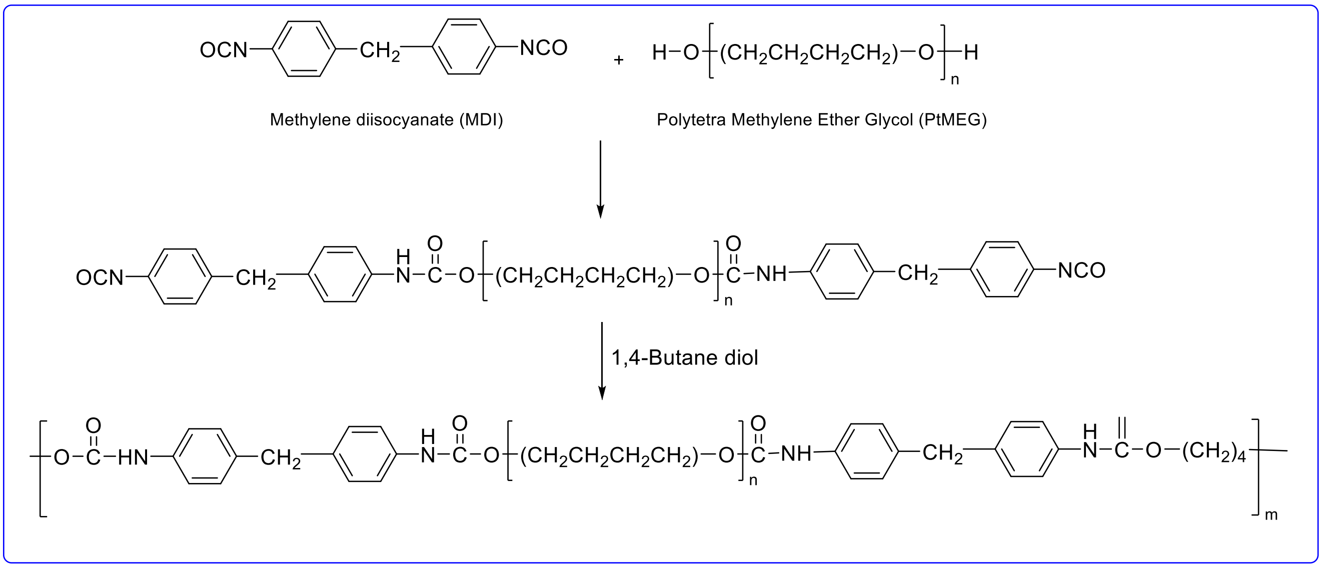

Fig. 8. Synthesis of Pellethane [100]

7.1. Safer aromatic isocyanates and potential alternatives

The electrophilic isocyanate (–N=C=O) is inherently reactive toward nucleophiles in biological systems, which underlies both the utility and the occupational/health risks of aromatic diisocyanates.

Creating safer isocyanate chemistry means either (A) designing new aromatic diisocyanates that retain desirable reactivity/selectivity while lowering volatility and biological reactivity, or (B) replacing isocyanates altogether with alternative chemistries that produce urethane-like linkages or comparable network properties.

Low-volatility, high-functionality isocyanates: Design bulky or oligomeric aromatic isocyanates (e.g., sterically shielded monomers, prepolymers) that reduce vapor pressure but conserve hard-segment stiffness. Investigate carbodiimide-modified MDI analogues or polymeric derivatives that present lower monomeric vapor release yet maintain reactivity to form networks.

Systematically measure gas-phase partitioning and reactivity toward small-molecule nucleophiles to correlate structure volatility/toxicity.

Masked / latent isocyanates with triggered unmasking: Develop blocking groups that are stable in storage but cleavable under benign stimuli (moderate heat, UV, specific catalysts) to minimize user exposure. Organic chemists can tailor blocking chemistries (oxime, carbamate, uretdione, imidazole adducts) to achieve controlled deblocking kinetics at curing temperatures while minimizing side reactions.

Isocyanate surrogates and non-isocyanate chemistries: Advance **non-isocyanate polyurethane (NIPU)** routes (e.g., cyclic carbonate + amine → hydroxyurethane) by improving monomer access and polymer properties. Focus on novel cyclic carbonate monomers prepared from biofeedstocks with tunable ring strain and reactivity.

Explore isocyanate surrogates produced using non-phosgene industrial routes—e.g., oxidative carbonylation pathways or urethane → isocyanate interconversions—optimizing for atom economy and safety. Investigate hybrid strategies where small amounts of highly reactive isocyanate are replaced by orthogonal click chemistries (thiol–ene, oxime ligation) to form comparable network topologies.

Reactive group "deactivation" after cure: Design post-curing quench chemistries that irreversibly consume residual –NCO (e.g., reaction with safe nucleophiles immobilized in formulation) to reduce leachables and post-processing hazard.

New monomers must match cost and scale expectations; synthetic routes should minimize hazardous intermediates (avoid phosgene). Regulatory acceptance requires toxicology testing; early screening assays for adduct formation with model nucleophiles or peptides can rapidly triage candidates.

7.2. Expansion into advanced technologies and functional devices

MDI/TDI-based platforms are well positioned to enter advanced markets (soft robotics, wearable electronics, energy devices) if molecular design can incorporate functional responsiveness, conductivity, and controlled mechanics without sacrificing manufacturability.

Stimuli-responsive networks: Introduce dynamic covalent chemistries (transcarbamoylation, disulfide exchange, Diels–Alder) at well-defined positions to create materials that are reconfigurable or self-healing. Design linkers whose activation conditions (temperature, light, redox) align with application constraints.

Implement orthogonal dynamic bonds: e.g., combine a thermally exchangeable backbone with a photo-reversible side chain for multistimuli control.

Conductive and electroactive PUs: Functionalize PU backbones or graft conductive oligomers/polymers (oligothiophenes, PEDOT oligomers) to provide intrinsic conductivity. Alternatively, covalently anchor conductive fillers to the matrix to improve percolation stability.

Tune soft segment polarity (ether vs carbonate) to balance ionic conduction (for electrolytes) and mechanical integrity.

Integration into microfabrication: Develop low-viscosity, rapidly curable precursors (e.g., UV-curable masked isocyanates, thiol-ene hybrid systems) compatible with additive manufacturing (SLA, DLP, inkjet). Tailor photochemistry to avoid radical-induced degradation of vulnerable polyols.

PU electrolytes & separators: Design polyether-rich soft segments with tailored Li-ion solvation environments and moderate crosslink density provided by aromatic hard segments (MDI) to maintain dimensional stability under battery operation.

Balance between functional additives and long-term stability (electrochemical, thermal) is crucial.

Device integration will require standardized testing for fatigue, cycling, and interfacial stability under operating conditions.

7.3. Integration with renewable feedstocks and green chemistry

Sustainable PU technology demands feedstock transitions (bio-polyols, biomass-derived diisocyanate surrogates), process intensification (milder conditions, solvent-free routes), and closed-loop life-cycle thinking. Actionable molecular and process strategies

Advanced lignin valorization**:** Develop selective depolymerization and catalytic upgrading to produce well-defined diol and polyol fragments with narrow functionality distributions. Target phenolic and aliphatic diols that can serve as soft/hard segment precursors.

Organic catalysis (hydrogenolysis, reductive cleavage with designed metal catalysts) and chemoenzymatic approaches can provide selectivity.

Tailored bio-polyols with controlled functionality: Engineer polyols from vegetable oils via regioselective epoxidation and controlled ring opening to produce mid-chain hydroxyls, enabling consistent soft segment behavior.

Develop protecting group strategies or selective transesterification to control primary vs secondary OH content, directly impacting urethane formation rates.

Non-phosgene isocyanate production: Support research into scalable non-phosgene methods (oxidative carbonylation, Curtius-related routes), optimizing catalysts and process safety. Evaluate life-cycle benefits and potential new impurities.

Process intensification and solvent minimization: Move toward waterborne PU dispersions and reactive extrusion to lower VOCs and energy demand. Chemists can design surfactants and stabilizers that are robust and biodegradable.

Design for recyclability: Build cleavable linkages (enzyme-cleavable esters or disulfides), or incorporate exchangeable bonds (vitrimer motifs), enabling either chemical depolymerization under mild conditions or dynamic reprocessing.

Bio-feedstocks are often heterogeneous — chemical refinement and standardization will be required for consistent polymer properties.

Technoeconomic analysis early in molecule design helps avoid dead-end monomers that are costly to produce at scale.

7.4. Opportunities for digital modeling and molecular design

Computational chemistry, machine learning (ML), and multiscale simulation can accelerate discovery by predicting reactivity, phase behavior, and structure–property relationships before synthesis.

7.4.1. Computational & data-driven directions

Quantum chemical modeling of isocyanate reactivity: Use DFT to quantify activation barriers for nucleophilic attack on different isocyanate isomers and masked variants. Map steric and electronic contributions to reactivity and regioselectivity (e.g., 2,4- vs 2,6-TDI).

Kinetic modeling of polymerization and side reactions: Develop mechanistic kinetic models (ordinary differential equations) incorporating catalysis, diffusion, and competing pathways (allophanate, biuret, uretdione). These models guide catalyst selection and process windows to minimize unwanted side products.

Molecular dynamics (MD) and coarse-grained simulations: Predict microphase separation, domain sizes, and mechanical response by simulating segmented copolymer architectures. MD can inform optimal block lengths and compatibilizer choices for target Tg and modulus.

Machine learning for property prediction and inverse design: Train ML models (random forest, neural nets) on datasets of polyol/isocyanate formulations vs measured properties (Tg, modulus, degradation onset) to enable inverse design: specify target properties → suggest monomer combinations.

Use active learning loops where experimental results update models to improve predictive power.

Integrated process-materials co-simulation: Couple reactor/process simulations (heat transfer, mixing) with kinetic polymerization models to predict molecular weight distributions and crosslink densities as functions of scale-up parameters.

8. Conclusion

Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) remain the backbone of the polyurethane (PU) industry due to their high reactivity, structural rigidity, and cost-effectiveness. Their chemistry - rooted in the electrophilicity of the isocyanate functional group and its selective reactivity toward nucleophiles - continues to enable a remarkable diversity of materials, from flexible foams and coatings to rigid insulation panels, biomedical devices, and emerging smart materials. At the same time, the intrinsic structure–property relationships dictated by diisocyanate isomerism, microphase separation, hydrogen bonding, and crosslink density underscore the profound link between organic molecular design and macroscopic performance. Despite these advantages, significant challenges persist. The toxicity and volatility of aromatic isocyanates, their environmental persistence, and the inherent difficulty of recycling crosslinked PU networks highlight the limitations of current MDI/TDI-based systems. Moreover, the sustainability of petrochemical feedstocks and the hazards associated with phosgene-based industrial production further emphasize the need for greener alternatives. Recent advances provide important signs of progress. Bio-based polyols, non-phosgene routes to isocyanates, and functional modifications (self-healing, shape-memory, flame retardancy) demonstrate how organic synthesis and catalysis can drive innovation. The integration of nanofillers and hybrid chemistries continues to expand the property envelope, while circular economy strategies and dynamic covalent chemistries (vitrimers) point toward reprocessable and recyclable PU networks. Biomedical research, meanwhile, is leveraging careful molecular tailoring to improve stability, biocompatibility, and targeted degradation. Looking ahead, the future of MDI/TDI-based PUs will be defined by the balance between **performance, safety, and sustainability**. Safer isocyanates and masked variants, scalable bio-based feedstocks, and advanced computational tools for predictive design will all play pivotal roles. For organic chemists, the greatest opportunities lie in developing selective catalytic pathways, reversible chemistries, and rational structure–function design principles that enable both high-performance and environmentally responsible PU systems.

Ultimately, progress in this field will hinge on a convergence of molecular-level innovation with process engineering, regulatory frameworks, and circular material strategies. By harnessing the flexibility of aromatic isocyanate chemistry while addressing its inherent risks, the next generation of polyurethane materials can deliver not only superior functionality but also greater alignment with the goals of green chemistry and sustainable development.

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