

Non-Isocyanate Polyurethane Foams. Part II

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Abstract: Polyurethane foams (PUFs) constitute a major class of polymeric materials, widely appreciated for their excellent mechanical strength, chemical resistance, and physical versatility. They are used in a wide variety of applications, such as insulation, cushioning, coatings, and structural parts. Traditionally, PUFs are prepared through polyaddition reactions involving polyols, diisocyanates, and water, where the in-situ generated CO₂ in the reaction mixture serves as the blowing agent. However, there are significant concerns with the use of isocyanates as they are toxic, classified respiratory sensitizers, and contribute to environmental pollution. These issues have directed both researchers and industry experts to search for safer and more sustainable alternative feedstocks.

The polyaddition reaction between cyclic carbonates (CCs) and polyfunctional amines has been one promising alternative. The reaction leads to the formation of non-isocyanate polyurethanes (NIPUs), specifically polyhydroxyurethane foams (PHUFs). Foaming is achieved by using external chemical blowing agents or through self-blowing reactions, where gases are generated directly in the system. The generated foam cells – the structures that give foams their unique properties – depends largely on the gas-forming reactions.

This review focuses on the different blowing agents used in NIPUF synthesis, such as poly(methylhydrogensiloxane) (PHMS) and liquid fluorohydrocarbons. It also looks at recent advances in self-blowing techniques, which eliminate the need for external agents and make the process more sustainable. Special emphasis is placed on NIPUFs derived from renewable feedstocks, as these align with global trend towards green chemistry and circular materials. The review provides an overview of both externally blown and self-blown biobased NIPUFs, detailing their synthesis, performance, and potential industrial applications. **Keywords:** nuclear power station, cooling systems, patents.

Keywords: biobased polyurethane, blowing agent, non-isocyanate polyurethane, polymeric foams, polyurethane foams, self-blowing.

Table 1. List of abbreviations used in this review

Abbreviation	Full term
CCs	cyclic carbonates
DABCO	1,4-diazabicyclo [2.2.2] octane
DSTD	dibutyltin dilaurate
DBU	1,8-Diazabicyclo[5.4.0]undec-7-en
EC	ethylene carbonate

Abbreviation	Full term
GC	Glycerol Carbonate
LDI	L-Lysine ethyl ester diisocyanate
MOF	metal-organic framework
NIPUFs	non-isocyanate polyurethane foams
NIPUs	non-isocyanate polyurethanes
PC	propylene carbonate
PHMS	poly(methylhydrogensiloxane)
PHUFs	polyhydroxyurethane foams
PHUs	polyhydroxyurethanes
PUs	polyurethanes
PUFs	polyurethane foams
ROP	ring-Opening Polymerization
SDGs	sustainable Development Goals
SOC	spiro-orthocarbonate
TBD	triazabicyclodecene
VOCs	volatile organic compounds

7. Catalysts for Urethane Formation in NIPU Synthesis

This section focuses on catalysts used in the reaction between cyclic carbonates and amines to form urethane linkages during the synthesis of non-isocyanate polyurethanes. Catalysts are crucial because they help speed up the reaction, improve selectivity, lower energy consumption, and support the development of more sustainable materials.

7.1 Overview of Recent Advances

Recent research has explored upcycling biobased polyurethane foams into thermoset networks. This approach helps promote sustainability by contributing to circular economy strategies. These foams are made from biobased polyols and

polyisocyanates and can contain up to 93% renewable carbon. Using dibutyltin dilaurate (DBTDL) as a catalyst, transcarbamoylation reactions allow reshaping PUFs into thermoset networks, making them recyclable [85,86].

Catalysts like DBTDL are key for enabling urethane bond exchange reactions, which create dynamic covalent networks. These networks show properties like stress relaxation and reprocessability, which are critical for developing recyclable thermosets from already-cured PUFs.

Biobased polyols such as Pripol® 2033 and diglycerol, when combined with L-Lysine ethyl ester diisocyanate (LDI) and Tolonate™ X FLO 100, have been used to make lightweight, high-performance foams with good thermal and mechanical stability [87].

Several patents illustrate the progress in this area:

- A bifunctional urethane acrylate monomer modified with organosilicon fragments was developed to improve coating properties such as flexibility, smoothness, and hydrophobicity. The presence of a non-isocyanate polyurethane backbone and reactive acrylate terminals enables fast drying, better adhesion, and reduced internal stress during curing. The monomer can be used in UV-curable and thermally curable systems. The synthesis is solvent-free and environmentally friendly [88].
- A polyurethane coating based on bisphenol AF and fluorinated cyclocarbonates was developed using CO₂ and perfluoro-epoxy compounds under high-pressure synthesis. The resulting nonisocyanate system exhibits excellent lyophobic and oleophobic behavior, combined with superior hardness, chemical durability, and anti-corrosion properties, offering potential as a high-performance alternative to conventional polyurethane films [89].
- This patent outlines the preparation of a gallic acid-based nonisocyanate polyurethane modified with siloxane segments. The process involves copolymerization of gallic acid-derived and organosilicon cyclic carbonates with

amine curing agents. The final polymer displays enhanced thermomechanical strength while being synthesized under mild and eco-friendly conditions without hazardous reagents [90].

- A nonisocyanate polyurethane coating was developed from sorbitol-based cyclic carbonates obtained via CO₂ cycloaddition to sorbitol epoxides. After blending with diamines or polyamines, the coating formulation demonstrated high hardness, impact resistance, and biodegradability. This material provides an environmentally safe coating option, suitable for replacing traditional isocyanate-based systems [91].

- A hybrid material combining nonisocyanate polyurethane and epoxy resin was developed through a crosslinking process. The resulting coating demonstrates strong adhesion, good mechanical strength, and chemical resistance – particularly against water, gasoline, and salt spray – making it suitable for protective painting applications [92].

- This Korean patent discloses a hybrid network polymer composed of cyclocarbonate- and epoxy-functionalized oligomers crosslinked with amine-terminated oligomers. The resulting polymer network shows a high gel content and structural uniformity. It is intended for use in composite matrices with controlled reactivity and multifunctional performance [93].

- A method for synthesizing nonisocyanate polyurethane is presented, using a novel catalyst system composed of metal salts and ionic liquids. The process allows for the formation of polycyclic carbonates, which are then reacted with amines. The technique offers high catalytic activity, selectivity, and process simplicity under mild reaction conditions [94].

- This invention outlines a two-step route to nonisocyanate polyurethane using renewable feedstock – epoxidized soybean oil and CO₂. The process yields cyclic carbonates that are further reacted with amines to produce environmentally

friendly NIPUs. It emphasizes low environmental impact, simplicity, and suitability for scaling up with bio-based resources [95].

7.3 Types of Catalysts

Catalysts play a key role in enabling the urethane-formation reaction between cyclic carbonates and amines during the synthesis of non-isocyanate polyurethanes. These reactions typically involve **aminolysis**, where nucleophilic amines open the cyclic carbonate rings to create hydroxyurethane linkages. The type of catalyst used can have a big impact on how quickly the reaction proceeds, how selective it is, and how sustainable the process can be overall.

Here's an overview of the main types of catalysts used in NIPU synthesis:

1) **Organobases** (like DBU, DABCO): These are effective at promoting ring-opening reactions under mild conditions, with good selectivity.

2) **Organometallic catalysts** (such as tin and zinc complexes): These can work well but raise concerns about toxicity.

3) **Ionic liquids** (especially imidazole-based compounds): Act both as solvents and catalysts, helping to improve reaction rates and selectivity.

4) **Enzymatic catalysts**: Offer a green alternative for urethane synthesis, operating under mild, bio-friendly conditions [96,97]

5) **Thiol-based systems**: Can act as both nucleophiles and catalysts, supporting decarboxylation reactions and urethane bond formation [97].

Table 7.1

Comparative Table of Catalysts for Urethane Bond Formation.

Catalyst Type	Examples	Reaction Conditions	Remarks
Organobases	DBU, DABCO	60–120°C, solvent-free	Low toxicity, fast, selective

Organometallic	DBTDL, Zn (II), Sn (IV)	80–150°C	Efficient, industrial use, moderate toxicity
Ionic Liquids	[BMIm][BF ₄], [EMIm][Cl]	70–130°C	Catalysis + solubilization
Enzymatic	Lipase, urease	<60°C, aqueous	Low toxicity, still in development
Thiol-based	Di-/Trifunctional thiols	Varied	Foam-specific, dual function

Catalytic systems for urethane formation in NIPUs are moving towards greener solutions that offer better recyclability and lower toxicity. Organocatalysts and thiol-based systems in particular show great potential for creating dynamic, reprocessible, and environmentally friendly polyurethane materials.

8. Types of NIPUF Foams and Blowing Agent Technologies

Non-isocyanate polyurethane foams can be classified based on their characteristics, such as density and thermal stability. A study by Monie et al. explores different types of foams, from microcellular to rigid foams, each designed for specific uses like thermal insulation or impact cushioning. One of the key features of these foams is their ability to self-blow – they generate CO₂ during the reaction between amines and thiols, which creates the foam structure. This process helps produce foams with good mechanical properties and stable cell structures [14,98].

The research also focuses on biobased self-blowing polyhydroxyurethane foams, which are classified as high-resilience flexible foams. What makes these foams special is that they generate CO₂ during synthesis, so there's no need for external chemical blowing agents.

Recent studies have focused on biobased self-blowing polyhydroxyurethane foams classified as high-resilience flexible foams. Adjusting the thiol functionality enables tuning of compressive strength and glass transition temperature (T_g). Moreover, these foams demonstrate reprocessability, making them recyclable without compromising performance [85].

Generally, NIPU foams are categorized as rigid, semi-rigid, or flexible based on formulation and processing. Since no isocyanates are used, foaming relies on in situ CO_2 generation during polymerization, eliminating the need for external blowing agents [71].

Other variations of NIPU foams, such as POSS-modified or flame-retardant foams, help expand their applications beyond typical uses – reaching areas like construction and even aerospace. Adding materials like Laponite or PDMS can further improve the foam morphology and cell structure, leading to better overall performance [99].

Table 8.1

Classification of NIPU Foams.

Foam Type	Properties	Applications	Blowing Mechanism
Rigid	High compressive strength, low flexibility	Insulation, panels	Self-blowing (CO_2 release)
Semi-rigid	Balance of strength and elasticity	Cushioning, structural foam	CO_2 + crosslink density control
Flexible	Low density, high elasticity	Furniture, packaging	In situ CO_2 generation

POSS-modified	Thermal and mechanical stability	High-performance insulation	Modified carbonate foaming
Flame-retardant	Enhanced fire resistance	Construction, automotive	CO ₂ + inorganic fillers

8.1 Foaming Agents for Non-Isocyanate Polyurethane Foams (NIPUFs)

Foam formation in NIPUs generally relies on either physical blowing agents (such as supercritical CO₂) or chemical agents that release gas during the reaction. Bourguignon et al. [80] demonstrated a water-induced self-blowing approach, where the hydrolysis of carbonates generates CO₂ in situ, eliminating the need for external blowing agents.

There is increasing research interest in soybean oil-based NIPU formulations as a sustainable alternative to conventional isocyanate-based foams [100]. Another common method is reactive foaming, where amines react with cyclic carbonates in the presence of catalysts to produce foams with well-controlled pore structures, as reported by Monie et al. [71].

Hybrid non-isocyanate polyurethane foams can be further improved by incorporating synthetic nanoclays as inorganic fillers. As shown by Chaib et al., the addition of such clays into self-blowing NIPU formulations enhances the cell morphology and mechanical performance of the foams, while also contributing to improved flame retardancy [101]. In another study, Kojić et al. demonstrated that increasing the fraction of spiro-orthocarbonate in photopolymerized aliphatic polycarbonate networks reduces the internal mechanical stress, as confirmed by a measurable decrease in birefringence [102].

To confirm that CO₂ was the primary foaming agent, Monie et al. [71] replaced water with heptane; no foaming occurred, verifying the essential role of CO₂. In another experiment, the gas released during the reaction was bubbled

through a calcium hydroxide solution, resulting in CaCO_3 formation and further confirming CO_2 generation.

In [101], the formation of PHU foams was achieved by mixing a diamine, a dithiol, and a tricyclic carbonate, resulting in stable foams. Raman spectroscopy confirmed the presence of thioether and urethane bonds.

Hybrid NIPU foam systems that incorporate synthetic nanoclays (such as Laponite) show improved cell morphology, enhanced stiffness, and better flame retardancy [101]. In a separate study, Valette et al. demonstrated that introducing amino-telechelic PDMS as a soft segment into bio-based NIPU formulations, combined with foaming using water and/or ethanol, enabled precise control over the foam structure. The resulting samples exhibited cell diameters ranging from 130 to 3090 μm and densities from 0.055 to 0.95 g cm^{-3} , with the PDMS content significantly influencing hysteresis, recovery, and firmness [103].

Table 8.2

Foaming Methods and Agents in NIPU Systems.

Foaming Method	Blowing Agent (Specific Chemical Name)	Advantages	References
Self-blowing (thiol-based)	Poly(methylhydrogensiloxane) + glycerol carbonate $\rightarrow \text{CO}_2$ in situ	No external blowing agents; dynamic bonding	[80]
Reactive foaming	Glycerol carbonate + hexamethylenediamine (HMDA) $\rightarrow \text{CO}_2$	Good cell structure control	[71]
Hybrid foaming with	Glycerol carbonate + HMDA + inorganic fillers (Laponite clay,	Enhanced mechanical	[101]

fillers	CaCO ₃)	and fire resistance	
Photoinitiate d foaming	Spiro[5.5]undecane-2,8-dione (Spiro-orthocarbonate, SOC)	Reduces internal stress	[102]

9. Applications of Non-Isocyanate Polyurethane Foams

NIPUFs are already used – and continue to be developed – for a wide range of applications across different industries. These include:

1. Construction and Building Materials
2. Automotive Components
3. Furniture and Bedding
4. Packaging and Consumer Goods
5. Biomedical Applications
6. Coatings and Adhesives
7. Environmental Remediation
8. Electronics and Functional Materials

Construction and Building Materials. In the construction sector, NIPUFs are widely applied in thermal and acoustic insulation panels, sealants, and gap fillers. Their combination of low thermal conductivity, minimal water uptake, and high dimensional stability makes them especially suitable for building envelopes and HVAC systems [18]. Bourguignon et al. [80] further demonstrated a water-induced self-blowing approach that produces NIPU foams with stable morphology and good insulating properties under ambient conditions, reinforcing their potential as eco-friendly building materials.

Automotive Components. In automotive manufacturing, NIPUFs are used for seat cushions, dashboard insulation, noise-damping materials, and lightweight interior panels. These foams maintain good mechanical strength and thermal

stability, and they withstand repeated heating–cooling cycles without significant degradation. Their potential for mechanical recycling also fits with current trends toward circular manufacturing [104].

Furniture and Bedding. NIPUFs are also used in furniture and bedding products, where they can be tailored for varying rigidity, softness, and flexibility. Their non-toxic nature is particularly important in household environments such as mattresses and upholstered furniture. When produced from renewable feedstocks like castor oil or soybean oil, these foams contribute to the environmental sustainability of consumer products [103].

Packaging and Consumer Goods. Protective packaging and certain disposable consumer products are emerging markets for NIPUFs. Biodegradable and compostable NIPU variants have the potential to significantly reduce plastic waste. NIPU-based coatings for paper packaging offer a sustainable alternative to polyethylene films, maintaining barrier properties while being more environmentally friendly.

Biomedical Applications. Wang et al. developed a photosensitive non-isocyanate polyurethane acrylate (NIPUA) resin specifically for 3D printing customized orthopedic surgical guides, demonstrating high tensile and flexural strengths, good thermal stability, low hemolysis rates, and cytocompatibility with MC3T3-E1 and C2C12 cells, as well as minimal inflammatory response in vivo—supporting its suitability for patient-specific surgical tools [105].

Coatings and Adhesives. NIPUs are employed in corrosion-resistant coatings with low VOC emissions. Waterborne and UV-curable NIPU coatings have been successfully applied to metals, ceramics, and wood, offering high hardness, weather resistance, and chemical durability – making them suitable for industrial environments [106]. NIPU adhesives derived from tannin or rosin derivatives are used in wood composites, automotive parts, and eco-friendly packaging [107].

Environmental Remediation. NIPU-based nanocomposite coatings incorporating surface-treated ZnO nanoparticles have demonstrated enhanced anticorrosive performance, likely due to the nanoparticles' ability to block microdefects and improve barrier properties. These coatings also show potential for antimicrobial activity, making them promising candidates for protective and filtration applications in contaminated environments [108].

Electronics and Functional Materials. Electronics and Functional Materials. Emerging applications of NIPU foams include lightweight electromagnetic interference (EMI) shielding and components for smart devices. Recent work demonstrates self-blown NIPU foams that, when loaded with conductive and magnetic fillers, achieve strong EMI-shielding performance while maintaining dimensional stability and mechanical resilience – highlighting their potential in flexible and wearable electronics [109].

Table 9.1

Applications of NIPUFs by Sector.

Sector	Application Example	Key Advantages
Construction	Insulation panels, sealants	Thermal stability, low water uptake, eco-friendly
Automotive	Seat foams, dashboards	Lightweight, recyclable, thermal durability
Furniture	Mattresses, cushions	Softness, non-toxicity, renewable-based
Packaging	Biodegradable packaging foams	Eco-friendly, compostable
Biomedical	Scaffolds, wound dressings	Biocompatible, non-toxic

Coatings	Industrial anticorrosive layers	UV-resistance, low VOC, waterborne
Adhesives	Furniture & panel bonding	Renewable, strong adhesion
Remediation	ZnO nanocomposites for filters	Antimicrobial, pollutant degradation

Conclusion

This review highlights the growing potential of non-isocyanate polyurethane foams as a safer and more sustainable alternative to conventional polyurethane materials. The analysis brings together current research on synthetic strategies, the use of cyclic carbonates, the role of various catalysts and amines, and the innovative approaches to foaming and material design. The relevance of this field is driven by the urgent need to replace hazardous isocyanates and transition to greener materials that align with global sustainability goals. NIPUFs offer unique advantages, including the use of CO₂ as a raw material, the integration of bio-based feedstocks, and the ability to develop recyclable and reprocessable foams with tailored properties. Despite the significant progress, challenges remain in scaling up these technologies, optimizing reaction conditions, and ensuring consistent material performance. However, the continued development of NIPUFs – supported by innovations in catalysis, polymer design, and foaming techniques – demonstrates their real potential to transform industries ranging from construction and automotive to biomedical and electronics. This review emphasizes that NIPUFs are more than just an academic curiosity: they represent a critical step toward safer, more sustainable polymer materials. The future of polyurethane chemistry will likely be shaped by these non-isocyanate systems, and further research will play a key role in unlocking their full potential.

Historical and Industrial Milestones

It's important to acknowledge the remarkable historical milestones in the development of non-isocyanate polyurethanes. The first industrial production of NIPUs was launched back in 1978 at the Sverdlov Plant in Dzerzhinsk, USSR. This achievement was based on the pioneering work of O.L. Figovsky and colleagues, documented in Soviet Author's Certificate SU 707258. It marked a key step forward in the global effort to create safer, greener polyurethane materials.

Decades later, this early innovation inspired further breakthroughs. In 2012, Eurotech Ltd. (USA) scaled up production under the scientific leadership of Dr. Oleg Figovsky, establishing two plants dedicated to manufacturing environmentally friendly NIPU-based products. This milestone was internationally recognized with the 2015 Presidential Green Chemistry Challenge Award from the U.S. Environmental Protection Agency, celebrating their significant contribution to sustainable chemistry [109].

These achievements show that NIPUs are not just a theoretical concept – they are a practical, industrially viable solution that bridges early scientific discovery with modern green chemistry innovation. They prove that it's possible to combine technical performance with environmental responsibility, aligning with global circular economy goals.

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