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ABSTRACT

This thesis describes a study of Non-Isocyanate Polyurethanes (NIPUs) which is a next generation sustainable polymer. It replaces conventional isocyanate based polyurethanes. It discusses the reaction mechanisms of the NIPU formation such as cyclic carbonate aminolysis, transurethanization, ring opening polymerization and carbon dioxide-epoxide (CO2 epoxide) coupling and then addresses the kinetic behavior, catalyst design and structure-property relationship of the NIPU formation. Advanced material architectures such as waterborne dispersions, epoxy/NIPU hybrids, UV-curable systems, and self-healing vitrimers are also critically analysed for their mechanical, thermal, and dynamic performance. Two unresolved industrial challenges that is foaming window control and closed-loop recycling are analysed through comparative studies of aromatic versus aliphatic cyclic carbonates and multi-dynamic bond networks (disulfide, imine, acetal) which enables solvent-free recyclability. The thesis further highlights toxicological profiles, circular-economy integration, and bio composite development using natural fibres (jute, flax, hemp, bamboo) which are reinforced with bio-based NIPU matrices. Finally, three conceptual innovations are proposed: a Reactive CO_2 Dual-Function (RCDF) platform for simultaneous carbon fixation and polymerization, lignin-derived bifunctional carbonate macromonomers for high-performance coatings, and NIPU-based bio adhesive hydrogels for wound closure and tissue repair. Collectively, this work forms a basis for a combined approach for transitioning NIPU chemistry from laboratory synthesis to scalable, circular, and non-toxic industrial applications.

Key words: Non-Isocyanate Polyurethanes (NIPU); Polyhydroxyurethanes (PHU); Cyclic Carbonate Amino lysis; CO_2-Epoxide Coupling; Transurethanization; Self-Healing Vitrimers; Covalent Adaptive Networks; Waterborne Polyurethane Dispersions

1. INTRODUCTION

Polyurethanes (PUs) are one of the most useful and adaptable polymeric material [1]. Globally, this is a widely used plastic. At global level the production exceeds over 25 million metric tons every year. We find them all over the place like building materials, car parts, medical equipment and everyday items. They also have good mechanical strength, chemical strength and structural adaptability. In 2023 the market of polyurethane was worth USD 49.5 billion and now it is expected to grow to USD 67.8 billion by 2028. This is because the consumer demand for these materials is very high. This is because they are strong, lightweight, and energy-efficient. This usefulness of this polymer has come from one main chemical reaction where we mix polyols, which have hydroxyl groups, with super reactive isocyanate groups (-N=C=O) [1]. PU widely used in thermal insulation, sealing, cushioning and structural applications highlights their industrial importance.

The basic chemistry has some problem. The main reactant use called diisocyanates like Toluene diisocyanate [TDI] and Methylene diphenyl diisocyanate [MDI] comes from process that uses phosgene ($COCl_2$). $COCl_2$ is one of the most poisonous chemicals which is used in factories. There groups like the European Chemicals Agency (ECHA)under Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) which tells that these poisonous compounds can really mess with our breathing and can even cause cancer. Diisocyanates are classified as carcinogenic, mutagenic and has respiratory sensitizing properties. There is need for complicated, dry storage and handling setups because these compunds also have extreme reactivity towards moisture.this increases both environmental and occupational risks. As a result, the polyurethane industry is under increasing regulatory pressure to use fewer or no isocyanates and this is causing a paradigm shift in favor of safer and more sustainable substitutes.

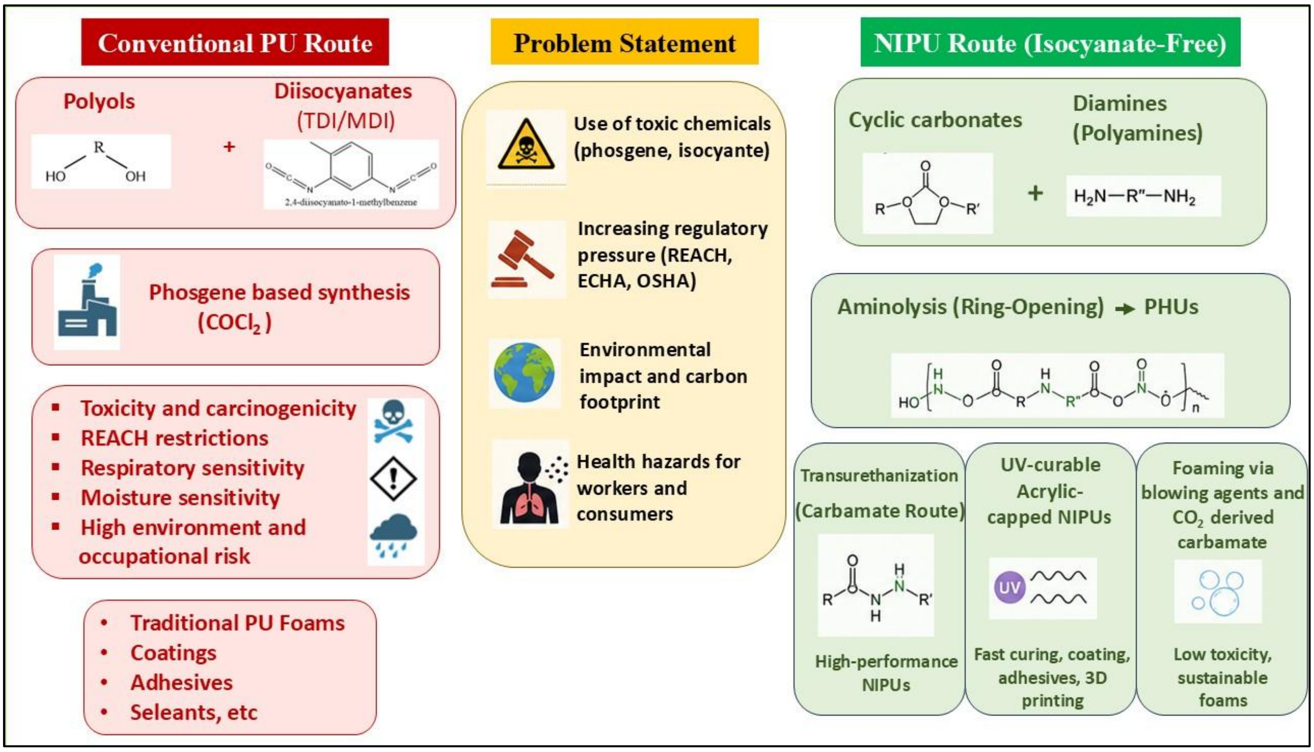
Regulations like REACH are really looking closely at MDI and TDI. They are also concerned about how much people can be exposed to them at work. Therefore, NIPUs, which used to be just an idea in labs but they are now becoming a real option for industry[2]. By mixing polyfunctional cyclic carbonates with di- or polyamines we can make NIPUs and this is the most promising way of synthesising them. All the atoms are used efficiently in this reaction and doesn't need solvents or $COCl_2$. It can even be done using materials from plants or by captured CO_2. By using CO_2 as a raw material, we not only reduce dependence on fossil resources but we also contribute to carbon capture. This helps in aligning polymer chemistry with circular economy principles. The first isocyanate-free route was reported by Dyer and Scott in 1957. Dyer and Scott demonstrated the feasibility of forming urethane linkages via aminolysis of cyclic carbonates. Since then significant progress has been made in catalyst development, reaction optimization, and feedstock diversification [3] [4].

There are several chemical processes that help in manufacture of NIPU. They involve (a) the transurethanization reaction involving dicarbamates and diols, (b) polyaddtion reaction which involves difunctional cyclic carbonates with diamines[5]. The second process is yield of PHUs and this has received considerable amount of attention because it is environment friendly and is simple to study [3] [6]. Traditional PUs have great strength due to their ideal blend of hard and rigid components and flexible and soft components. PHUs lack the ability to distinguish between these two elemnents. Hydroxyl groups (-OH) forms part of PHUs. This group make the material stable and at the same time they also act like microscopic buckles. Too many internal bonds are being created which lock the structure in place. Hence, the molecules become fixed and they cannot interact freely to form longer, stronger chains. This leads to result where the final product have low molecular weight which means it is less mechanically durable compared to conventional plastics. The new material do not require the PHU technique instead scientists are using an alternative technique known as transurethanization. As a result, such materials are as effective, strong and durable as common PUs [7]. This approach allows for easier integration of various natural components, suchas castor oil, sugarcane processing leftovers and other biorefinery products [8]. Utilizing such natural resources allows for a more straight forward way to create polymer compounds that degrade in nature [6].

Even though it has been promising, the transurethanization is still not being used in industries. It takes very hars and intense conditions to get the molecules to join together to form long strong chains. It also poses a challenge in being able to obtain high molecular weights in mild conditions. In order to find a remedy for this, scientists are blending PHUs with other commonly used plastics such as epoxy, acrylic, or silicon [9]. Therefore, veryone shifted focus to hybrid NIPU systems [10]. Its more like combine them all and enjoy the best of both worlds. It strengthens the final product, makes it more adhesive and is so easy to shape and Mold in factories [7]. Thanks to these enhancements that these new hybrid plastics are nowcapable of being applied to industrial coatings, super-glues and even 3-D printing for the first time. To begin with, a simple NIPU is synthesized via the traditional chemical route, called aminolysis. Further, the researchers alter the formula chemically by incorporating an acrylic component (methacrylic anhydride) into the structure of the polymer [11]. The resulting compound is particularly notable for the ability to instantly cure and solidify under ultraviolet radiation exposure. This helps make this substace ideal for industrial applications such as coating products and even printing then in three dimensions. These kinds of discoveries represent a huge milestone in research since this opens door for practical application of the matrial in industrial production facility.

The chemistry of solid plasticsis under study while the commonplace PU foam field is also in a huge change. The traditional foam is formed through a quick recation between polyols andtoxic isocyanates that releases heat. Typically a bit of water is added to this mix by manufacturers. The water instantly reacts with the isocyanates, causing the CO_2 gas to be released immediately into the liquid and expanding it into foam. This technique is very effective and very fast. But it leaves factories reliant on hazardous, toxic chemicals. New NIPU foam technologies provide a far less harmful and environmentally friendly means of obtaining that puffiness. The new approaches remove the need to use toxic chemicals, instead there is use of 'physical blowing agents' (trapped gasses) or specially cyclic carbonates which are synthesized using captured CO_2 [12]. These new methods help to completely get reduce of toxic ingredients. They even open the door to creating foams that are easily recyclable and made from natural, bio-based materials. Trneds for the development of isocyanate-free PU systems can be seen from the increasing interest in the industry and academia. In dustrial companies like Evonik Industries, Wanhua Chemical Group, Perstorp Holding AB, Huntsman Corporation, as well as research projects funded by Horizon like the NIPU-EJD consortium, are working on NIPU coatings, foams, elastomer, adhesives and vitrimer. It is expected that by 2032, we will observe a growth rate of about 9%.

The purpose of this research is to push eco-friendly plastic technology forward by introducing the most up-to-date non-isocyanate chemistry directly to the industrial paint and coating market. It focuses on preparing acrylic-capped NIPU building blocks (prepolymers) using the transurethanization method. Safe and sustainable ingredients are used in this method and hazardous, chlorine-based chemicals are completely avoided. The newly created NIPU building blocks are then combined with standard, commercially available acrylics (diacrylates). On combination it helped the researchers to easily adjust stretchy, strong, or sticky the final coating . The ultimate goal is to develop green coatings that can perform just as well as the traditional polyurethane-acrylic blends used today. Through this, the study will help to bring eco-friendly plastics out of the lab and onto real factory lines, making NIPUs a building block for next-generation green materials. This paper brings together what we've learned from lots of recent studies in areas like how to make these materials, how to give them different properties, foaming, looking at their whole lifespan, their safety, and how they fit into a circular economy. It goes further than just describing the chemistry.



2. FUNDAMENTAL CHEMISTRY OF NIPU

2.1 The Aminolysis Mechanism: Cyclic Carbonate Ring-Opening

The nucleophilic ring-opening addition of polycyclic carbonates by polyamines is the basis for NIPU synthesis. It is a mechanistically and product-architecturally different pathway from all isocyanate-based routes. In a typical polyisocyanate reaction, the isocyanate group (–N=C=O) group undergoes electrophilic addition to a nucleophilic alcohol group (–OH) from a polyol to create a urethane bond with no pendant functional groups. However, in the aminolysis pathway the nucleophile is the primary amine group (–NH2) and it attacks the electrophilic carbonyl carbon (C=O) in the strained 5-membered cyclic carbonate ring.

The ring opening splits the O-(C=O)-O linkage of the carbonate. The oxygen atom of the ring is retained along with its hydrogen atom. As a result, a free hydroxyl group (–OH) is present next to the newly created urethane linkage (–NH–C(=O) –O –). Therefore, the resulting polymers are structurally unique in that they are classified as PHUs, and not classical polyurethanes (PUs), reason being each urethane linkage is bordered by a primary or secondary pendant hydroxyl group. Therefore, we can say that, all NIPU materials are built on the hydroxyurethane unit, and this unit also gives them their distinctive mechanical, surface, recyclable, and physical characteristics.

In many chemical reactions, some atoms get lost as by-products (like water or CO2). Here, nothing is wasted. Every atom from the starting materials, that is from the cyclic carbonate and the amine ends up in the final polymer backbone chain. As a result, the reaction is a 100% atom economy step-growth polyaddition reaction. This makes the chemistry especially suitable for foam and coating applications where void-free, bubble-free cure is essential.

2.2 CO_2: A comonomer in cyclic carbonate synthesis

We first need special ring-shaped molecules called cyclic carbonates (5CCs) to make NIPU. They have naturally “strained” rings and it makes them easy to open up and react without needing high heat or pressure. First we take epoxides, then we add CO_2, using smart catalysts. The CO_2 added gets locked into the ring structure. This is how a greenhouse gas gets turned into a useful raw material in this process. This process is a great example of carbon capture and utilization (CCU). We store CO_2 inside new material, instead of letting it get wasted.

Plant oils such as sunflower, linseed, soybean, cardanol and castor oils are useful for making epoxy materials. These oils can be used to replce epoxides, which are made from non-renewable resources. By combining these plant-based epoxides with CO_2 and adding the appropriate catalysts (ionic liquids, metal-organic frameworks or even organic catalysts that re able to perform two functions simultaneously), the CO_2 is converted directly into a cyclic carbonate ring. The catalysts themselves havr improved a lot. The harder ones, such as metal-halides, required severe conditions. Now, we have newer plant-derived organic provides new sources of raw materials and stores carbon. Not so much of dependence is required on petroleum for the basic building blocks that we need. Apart from vegetable oils, researchers have found a growing number of other plant-based materials that can be turned into epoxies. These include terpenes (like limonene and myrcene) and substances from lignin, tannin and vanillin along with glycerol carbonate, isosorbide, sucrose, and chitosan structures. Each of these different materials add its own unique characteristics. For example terpenes and tannins provide stiffness, lignin and vanillin contribute their aromatic properties, while fatty acids offer flexibility and sugars give many reactive sites. This variety helps us precisely adjust the structure of the final NIPU material that we create.

2.3 Ring-opening Polymerization (ROP) through Azirridines

This process is an old process. It works by opening up small ring molecules called cyclic carbamates, especially aziridines (three-membered rings). The reaction can be started by heat or by a base (like sodium hydride, NaH, or N-acetylcaprolactam). The typical conditions include temperature around 200°C, initiators like NaH or N-acetylcaprolactam, and the ring size should be around 3-7 membered cyclic carbamates. The reaction type is Base- initiated or thermal ring opening. The initiator attacks the carbonyl carbon in the cyclic carbamate ring. The ring opens, forming a carbamate anion that can link to other rings. The chain grows by repeating this ring-opening step. The reaction stops when a chain stopper or proton transfer occurs. Two competing side reactions weakens efficiency: back-bitting cyclization where the chain folds back and recreate small rings (undesired), and CO_2 loss which creates unwanted amine segments.

Main technical challenges are given in this tabular form:

Challenges	Technical details
Toxic precursors	3 membered Aziridine ring (ethylenimine) is a probable human carcinogen (IARC Group 2A) and a mutagen. Cyclic carbamate monomers are often made using phosgene, a highly toxic gas.
High processing temperature	Needs 180–220°C, which increases energy use and can degrade bio-based materials.
No green synthesis route	Bio-based aziridines (from amino alcohols via cyclization) are multi-step, low-yield, and not scalable.
Poor molecular weight control	Dispersity (Đ) = 1.8–3.5, meaning polymer chains vary widely in length.
Limited functional group	Groups like esters, aldehydes, thiols in natural monomers interfere with the base initiators used for ROP.

Table 1. Key Challenges in Ring-Opening Polymerization of Cyclic Carbamates for NIPU Synthesis

Even though the chemistry works, these issues especially toxicity, high energy demand, and poor control make it unsuitable for large-scale, green production of NIPUs. Therefore, it is not commercially viable. To make this process greener and safer, researches focusing on phosgene-free synthesis routes, bio-derived cyclic carbamates, and dimethyl carbonate (DMC) or CO_2 – based carbonylation of amino alcohols are ongoing. These approaches could remove the main barriers and make green ROP of NIPUs possible.

2.4 Polycondensation

Polycondensation routes for NIPUs include AB-type self-condensation of acyl azides and transurethanization of carbamates with diols. Both methods are technically feasible but face limitations: acyl azides inevitably generate isocyantes as intermediates and transurethanization requires careful catalyst choice and temperature control to achieve high molecular weight.

2.4.1 AB-Type Self-Condensation

It is also known as the acyl azide pathway. The key chemistry is that a single monomer carries both a hydroxyl group (-OH) and an acyl azide ($-CON_3$). These react with each other in a self-condensation pathway. The preparation of acyl azides can be done by two ways: (a) from sodium azide + acyl chlorides/carboxylic acids, activated with chloroformates, (b) from hydrazine derivatives, oxidized from esters. In the mechanism the acyl azide unders=goes Curtius rearrangement, producing an isocyanate intermediate, which then reacts with hydroxyl group to form urethane linkages. Since the isocyanate formation is unavoidable therefore, it undermines the claims of “non-isocyanate”. Apart from this the Curtius rearrangement requires high temperatures (≥180 °C). Safety concerns also persist as as acyl azides are unstable and potentially explosive.

46

2.4.2 Transurethanization

It is also known as Transcarbamoylation. The key chemistry is an alcohol reacts with a carbamate to form urethanes. In the mechanism we first synthesise diurethane monomers via isocyanate and hydroxyls, or via amines and carbonates with base. Then the reaction proceeds with diol in the presence of catalysts. Catalysts such as Potassium tert-butoxide (KOtBu), alkali metal alkoxides, or organocatalysts are used. We also get a low molecular weight alcohol, mainly methanol or ethanol as by-product. There have been recent advancements like synthesis of high-molecular weight NIPUs (Mn up to 95 kg mol^{-1}). This is achieved at 120-150 **°C** with optimized alcohol/carbamate ratios and stepwise heating. Then there are renewable diols like polyethylene glycol (PEG), pentanediol, dodecanediol, lignin-derived diols which allow tunable thermal properties such as semi-crystalline behaviour, DSC/TGA stability.

2.5 Comparison of NIPU Synthesis Routes

While cyclic carbonate aminolysis dominates the field, three additional non-isocyanate synthetic pathways have been pursued:

Synthesis Route	Advantages	Limitations	Primary Applications
Cyclic Carbonate + Amine (Aminolysis)	100% atom economy No byproduct Bio-based Phosgene free	Slow kinetics Low Mn Hydroplasticization	Dominant route Most industrially viable
Polycondensation (Transurethanization)	Bypasses isocyanates Adaptable to DMC or Urea as carbonyl source	Phosgene derived intermediates historically used Releases methanol by-product Energy intensive	Coatings and adhesives Vacuum processing required
Ring-Opening Polymerization (ROP)	No by-product Well controlled molecular weight	Phosgene-required monomer historically High processing temperatures	Limited academic adoption Industrial barrier remains
Rearrangement (Curtius/ Lossen/ Hofmann)	Avoids isocyanates Accesses diverse urethane structures	Acyl azide precursors are explosives Laboratory scale only	Speciality fine chemicals Not suitable for commodity foams or coatings

Table 2. comparative overview of the four main NIPU synthesis routes

3. Methodology and Synthesis Protocols

3.1 Standard Aminolysis Protocol

The typical process for making NIPU usually involves four steps [2]. Firstly, the bio-based fatty acids or vegetable oils are converted into epoxides throught peracid expoxidation. Thereafter, these epoxides react with CO_2 under pressure (10-60 bar) and moderate heat with temperature around 80–120 °C in the presence of catalyst to form cyclic carbonate monomers. In the third step, the cyclic carbonate is mixed with a stoichiometric or slightly excess amount of polyamine, usually without any solvent [13]. Finally, the mixture is heated at 80–140 °C for 2–24 hours, allowing the aminolysis reaction to build the polymer network [13].

Catalysts play a crucial role in the carbonate formation step. Catalysts which are usually used are quaternary ammonium salts, imidazolium ionic liquids, and dual systems such as ammonium iodide with TBAB (tetrabutylammonium bromide) [14]. More advanced metal-free organocatalysts have also been developed to accelerate the CO_2–epoxide coupling under milder conditions [15]. An interesting fact is that, the aminolysis step itself usually proceeds without a catalyst, but adding organocatalysts such as DBU (1,8-diazabicyclo [5.4.0] undec-7-ene), TBD (1,5,7-triazabicyclo [4.4.0] dec-5-ene), or thiourea derivatives can significantly speed up the reaction [11].

There is an important alternative where there is use of thiol-ene chemistry. In this thiols or cyclic dithiocarbonates are copolymerized together with amines and carbonates [16]. This produces a unique polymer network called Non-isocyanate poly(thiourethane) (NIPTU). Due to a sulfur-assisted mechanism, it is possible to decrease curing times considerably from hours to minutes using such a recation system and help in making fast setting coatings and adhesives [12].

3.2 Waterborne NIPU (WNIPU) Synthesis

Waterborne NIPUs are meant to substitute solvent-based PUs and lower Volatile Organic Compounds (VOC) emissions in coatings, adhesives, and paints. Based on the recent studies, there are basically three main classes and those are cationic, anionic, and non-ionic [17]. Each of these classes have distinct chemistry for dispersing in water. New advances include hybrid systems with bio-based monomers, nanocellulose stabilizers and improved adhesion properties.

PHU prepolymers that have terminal amine groups form Cationic WNIPUs. Then they are neutralized with organic acids (e.g., acetic or lactic acid) [18]. These polymer chains formed have positive charges which stabilize them in water. Scientists are working on new bio-acids and ionic liquid neutralizers for improved stability and lower costs.

Anionic WNIPUs are produced by converting amine end groups into carboxylic acids using anhydride modification and the subsequent neutralization with triethylamine. The resulting polymer chains formed have negative charges and are easily dispersed in water. Research shows that isosorbide derivatives (from glucose) are more adherent and cohesive in coatings and still water-dispersibility [19].

Non-Ionic WNIPUs are produced by grafting polyethylene glycol (PEG) or mPEG-NH_2 segments to carbonate building blocks. This class of polymers dissolve directly in water and has no charges. If we look into the current trends in research, the PEG-modified systems are now being developed as hybrid systems with epoxy systems for improved toughness and elasticity.

The epoxy systems with isosorbide-based have shown imporved adherence and cohesiveness in coating, and therefore they are ideal for industrial paints [19]. The cellulose nanocrystals can be used as stabilizers for fluorescent WNIPU latexes and this helps in improving dispersion stability and add functional properties like fluorescence.

3.3 Epoxy and Unsaturated Hybrid Systems

In the case of aminolysis of cyclic carbonates alone, the average molecular weight of the resulting molecules is generally very low, around 10,000 to 20,000 Daltons [7]. That’s way lower than the 40,000 to 80,000 Daltons we normally see with regular PUs. These smaller molecules are as strong though and people have come up with a couple of ways to combine it with other stuff. Some of these hybrid approaches are:

(i) Epoxy Hybrids : These are named as Routes A, B_1, B_2, or C): Oils that have been treated with epoxy are taken and then partially turned them into carbonates [9]. This gives us unique building blocks that contain both epoxy and cyclic carbonate parts. A kind of double network is formed as the polyamines link these two parts simultaneously. The epoxy part hardens fast and makes the material firm and stiff. The cyclic carbonate part uses aminolysis to ease any stress that builds up during hardening and this is due to its flexible hydroxyurethane sections.

(ii) Hydroxyurethane Methacrylates, or HUMAs: Opening up single cyclic carbonates using amines is the first step. Thereafter we add methacrylic anhydride to them. We get liquids that aren't too thick and when exposed to UV light they harden very fast often in just seconds. Therefore they become appropriate for machines like 3D printing and glues that need to set quickly for strong bonds.

(iii) NIPTU Systems: Bringing in thiols or cyclic dithiocarbonates help create a combined network of thioether and urethane [20]. This helps in speeding up the chemical reactions. On top of it, it gives the bonds a much better ability to swap out and reform which is great for recycling [21].

4. Recent advancements

4.1 Foaming Technology

First synthesis of NIPU foam was rwported by Adrien Cornille et al in 2015. Poly(methylhydrogenosiloxane) was used as blowing agent. This blowing agent was prepared to react with diamines and it released H_2 gas. The obtained NIPU foams showed thermal stability above 300 **°C** and glass transition temperature between 18–19 °C [22]. The mix of water and isocyanate creates CO_2 gas right inside the material, which helps it foam up. Its hard to use NIPUs for things like insulation and soft cushions as NIPU do not follow this pathway. In order to tackle the above two ways have been researched upon [6]:

(i) **Physical Foaming:** Assume there is a plastic NIPU material which is immersed in in very high-pressure CO_2 (the "supercritical" kind) [23]. The pressure is then rapidly reduced, resulting in numerous tiny gas bubbles forming within the polymer making it a foam. For this we need to ensure that viscosity and gelation of the material occur at the appropriate time when the gas begins to expand. Otherwise all these bubbles simply evaporate or merge with each other. In order to avoid this additives such as silicone fluids (surfactants) and clay nanoparticles can be used [24].

(ii) **Chemical and Self-Blowing Methods**: in this method, the generation of the gas takes place through chemical reactions [25]. For example one of the chemicals used is called Polyhydromethylsiloxane (PMHS) which releases hydrogen gas during reactions with certain amines. The second chemical is azodicarbonamide (especially when mixed with zinc oxide) produces nitrogen, carbon monoxide, and ammonia gas [23]. This occurs when the NIPU is heating up to cure. Another way is the formation of "carbamate salt intermediates" [12] which are generated before by using some amount of CO_2. During curing of the foam, the carbamate salts releases CO_2 gas [12]. It is important that the rate of the gas matches the rate at which NIPU cures [26].

Foam Type	**Monomers/Precursors**	**Diamine/ Catalyst**	**Blowing Agent**	**Key Properties/ Applications**	**Refrences**
CO_2-based foams (supercritical CO_2)	Cyclic carbonates (from CO_2)	Amino-telechelic oligoamide	CO_2 (monomer + blowing agent)	Low thermal conductivity, strong insulation, long-term applicability	[27]
100% bio-based flexible foams	Trimethylolpropane-based cyclic carbonate blends (rigid + flexible)	Hexamethylenediamine (HMDA)	Solkane 365/227 (fluorohydrocarbon)	No ozone depletion, improved pot life & gelation time, automated seating foams	[28]
Room temperature foams	Trimethylolpropane tris-carbonate + polypropylene oxide bis-carbonate	Ether diamine (Reactive) (EDR)	poly(methylhydrogenosiloxane)	Encouraging thermal insulation	[22], [29]
Glucose-based foams	Glucose-derived cyclic carbonates	HMDA + KH560 (silane coupling agent)	$NaHCO_3$	Elastic cell walls, limited fire resistance (needs flame retardants)	[31]
Self-blowing glucose foams (RT)	Glucose-based cyclic carbonates	HMDA	Maleic acid (initiator) + glutaraldehyde (crosslinker)	Rigid foams, good compression, tunable density via initiator/crosslinker ratio	[31]
Mimosa tannin-based foams	Tannin + cyclic carbonates	Diamines	Citric acid + glutaraldehyde	Open-cell morphology, higher glutaraldehyde → better compressive strength; higher citric acid → larger foam cells	[24], [32]
Tannin-substituted glucose foams	Glucose + condensed tannin	HMDA	Self-blowing	Improved fire retardancy (LOI 17.5–25.5%), reduced thermal stability	[33], [34], [35]

Sorbitol-based foams	Sorbitol biscarbonate	Cadaverine (lysine-derived diamine)	None (solvent-free)	Rigid foams, solvent-free synthesis	[34]
Amine–CO_2 adduct foams	Amine–CO_2 adducts + cyclic carbonates	Amines	CO_2 released in situ	CO_2 desorption up to 87% at 60 °C, low density foams (0.203–0.239 g/cm^3), in situ CO_2-blown foams	[29]
Xylose-based foams	Xylose-derived cyclic carbonates	Diamines	Self-blowing	Synthesized at ambient temperature, no sophisticated setup required	[36]

Table 3. Key Types of NIPU Foams, Their Synthesis Routes, and Properties

4.2 Smart and Self-Healing Materials

The emergence of self-healing and recovery of NIPUs is an important achievement for sustainable polymer chemistry. The NIPUs are different from traditional polyurethanes. NIPUs have been created from cyclic carbonates and polyamines with many hydroxyl groups and urethan bonds that provide flexibility. Due to the mentioned peculiarities, NIPUs possess a structure similar to vitrimers where a chemical network can be rearranged by transcarbamoylation at the temperatures higher than topology freezing transition temperature (Tv) [37]. As a result, NIPUs can adapt their network structure, enabling shape memory, crack repair, and closed-loop recyclability [37].

Dynamic covalent chemistry primarily governs self-healing in NIPU [38]. The Transcarbamoylation (urethane exchange) allows reversible bond reshuffling at elevated temperatures [39]. The imine bonds facilitates reversible condensation/ decondensation processes. The disulfide bonds allow fast exchange reactions to occur under mild reaction conditions [38]. Combining these two dynamic bond systems in Dual Dynamic Covalent Adaptive Networks (DDCANs) results in much more effiecient healing and recyclability [40]. This allows for NIPUs to heal any existing cracks in their material, restore their mechanical properties and be recycled multiple times.

As for the current advances in this field, there are bio-based Priamine 1075+p-phthaladehyde elastomers, crosslinked with tetrafunctional cyclic carbonates and extended with cystamine. Such materials have tensile strength of 3.22MPa and elongation at break of 234%. They also achieved 97.5% healing efficiency after 24 h at room temperature [40]. Reprocessing cycles restore tensile strengthof such materials up to 80.2%, 125.1%, and 136.1% of the original after one, two, and three cycles, respectively [37]. There are also Linseed oil-derived smart NIPUs with disulfide-containing amines and cyclic carbonates. These materials features adjustable stiffness and elasticity and excellent recovery during reprocessing. Their applications can be found in self-healing coatings and smart materials [41]. The review articles from 2024-2025 confirmed the rapid develipemnet of self-healing NIPUs due to bio-based precursors (glucose, sorbitol, lignin, tannins) and dynamic covalent networks [42]. They also highlighted applications in coatings, elastomers, flexible electronics, and biomedical hydrogels and reported healing efficiencies consistently above 90–95%, with multiple reprocessing cycles possible [42].

4.3 Functionalization Strategies

The performance capabilities of basic NIPU matrix is significantly broad because of physical and chemical functionalization. The polymer network can be tailored for better mechanical strength, hydrophobicity, biocompatibility, or degradability by introducing specific functional groups or additives [7]. These modifications influence the molecular structure through mechanisms such as ionic crosslinking, hydrogen bonding, surface roughening, or chain integration, thereby optimizing the material for specialized applications ranging from biomedical coatings to flexible electronics [2], [6].

Modifier	Mechanism	Performance Impact	Application Target	Refrences
Azetidinium Groups	Introduce both physical and covalent crosslinks through ionic bonding, strengthening the polymer network.	Achieve a glassy modulus ($E' \approx$ 2638.6 MPa) and complete *E. coli* eradication, indicating strong antimicrobial activity.	High-barrier medical wound dressings and antimicrobial coatings.	[43], [44], [45]
TiO_2 Nanoparticles	Create surface roughness and a hydrophobic interface, improving interfacial adhesion and durability.	Increase contact angle to 105.4°, enhancing water repellency and tensile strength.	Self-cleaning coatings and corrosion-resistant barriers.	[46]
Carboxymethyl Cellulose (CMC)	Reinforce hydrogen bonding and hybridize with biopolymers, improving cohesive strength.	Yield high tensile modulus and optimized water-vapor transmission rate (WVTR).	Breathable wound dressings and biocomposite films.	[47]

Phosphorylation	Imparts water solubility and aerobic biodegradability through phosphate incorporation.	Enables up to 50 % phosphate loading and dispersion in aqueous media.	Biomedical dispersions and environmentally degradable coatings.	[48]
PEGDA (up to 12 wt %)	Integrates flexible ether chains, enhancing elasticity and hydrophilicity.	Provides optimal tensile properties at 12 wt %; excessive loading leads to degradation.	Hydrogels, tissue scaffolds, and membrane coatings.	[43], [49], [50]
Thiol-ene Systems	Promote quasi-crystalline packing and reduce stiffness via dynamic thiol-ene linkages.	Exhibit modulus around 1.2×10^7 Pa with high flexibility.	Elastomers, flexible packaging, and wearable devices.	[16], [21]

Table 4. Functionalization Modifiers, Mechanisms, and Performance Outcomes for NIPU Systems

5. Research gaps and Objectives

Significant progress in the development of NIPUs has already made and are ongoing as well, but several critical challenges still exist. Such obstacles make it difficult for NIPU to move from the lab to industry.these challenges include baicis reaction kinectics. Material durability, molecular weight limitations, the sustainability of feedstock, process control and end-of-life management. The following gaps summarize the current state of knowledge and highlight opportunities for further research:

5.1 Reaction Kinetics

Aminolysis of five-membered cyclic carbonates is intrinsically slow and involves hours to days in typical conditions. This is completely at odds with the fast production times in industrial processing of PU. Organic catalysts like TBD and DBU have been demonstrated to improve conversion, but a scalable and non- toxic catalyst solution has not yet been found. The goal is to explore new systems of catalysts and other carbonate structures (such as six-memebered ring cyclic carbonate)to obtain industrially comparable reaction rates.

5.2 Hydroplasticization

The pendant hydroxyl are advantageous for adhesion and recycling also makes NIPUs hygroscopic. The glass transition temperature (T_g) drops and the mechanical properties are weekenedby water absorption. Recent tests have indicated that these clusteroluminescent NIPU films can provide real-time monitoring of softening with humidity, however systeman=tic, long term durability test data is missingin outdoor environment. The the aim is to create hydrophobic modifications or hybrid systems to overcome water sensitivity and to complete extensive durability testing under humid and outdooe conditions.

5.3 Molecular Weight Ceiling

Number-average molecular weights of NIPUs is usually (Mn) of 15–25 kDa which is significantly lower than conventional PUs which is (40–80 kDa). This somehow limits tensile strength, toughness, and elastomeric performance. Transurethanization strategies have achieved Mn values up to 95 kDa, but often require high energy inputs. Objective is to explore bio-based chain extension and post-polymerization strategies to achieve higher molecular weights under sustainable conditions.

5.4 Life Cycle Assessment and Techno-Economics

Existing LCAs and techno-economic analyses are fragmented and based on idealized laboratory-scale protocols. Comparative industrial data against conventional PU benchmarks are lacking. Recent studies have reported minimum selling prices of USD 3.15–4.39/kg for biomass-derived NIPUs, with reduced greenhouse gas emissions, but standardized methodologies are absent. Objective is to conduct full cradle-to-grave LCAs and techno-economic studies to establish industrial benchmarks for NIPU sustainability and cost competitiveness.

5.5 Foaming Window Control

Matching gas generation rates from chemical blowing agents with NIPU viscosity and gelation remains poorly controlled, leading to inconsistent foam morphology. While controlled epoxy functionality has enabled rapid self-blown foaming, systematic foam science comparable to conventional PU literature is missing. Objective is to develop controlled foaming protocols and establish a processing science framework for NIPU foams.

5.6 Closed-Loop Recycling

The demonstrations of dynamic covalent network (CAN) recyclability and foam-to-film conversion done in labs are promising, but industrial-scale recycling methodologies are yet to be develped. Current technology readiness levels are low (TRL 3–4). Therefore the goal is to scale up recycling strategies to TRL 6 and establish standardized closed-loop recycling pathways for NIPUs.

5.7 Six-Membered Cyclic Carbonate Chemistry

The six-membered cyclic carbonates (6CCs), compared to their seven-membered counterparts, have higher degree of ring strain and exhibit high rates of reaction by nucleophilic substitution (aminolysis). Unfortunately these compounds have yet to be studied due to the possibility of homopolymer formation. Design rules for achieving stability/ reactivity balance in 6CCs remain unknown.

5.8 Biobased Diamine Availability

The majority of NIPU studies rely on petroleum-derived diamines such as HMDA, IPDA, and EDA. Bio-based diamines from fatty acids and Priamine™ have been reported but the diversity and scalability of renewable diamines still remains limited. Objective is to expand the library of bio-derived diamines from amino acids, lignin, and algae to strengthen the sustainability profile of NIPUs.

Gap	Technical Challenege	Existing studies / attemots	Key findings	Industrial readiness	Research oppotunities
Reaction Kinetics	Aminolysis of 5-membered cyclic carbonates is slow (24–72 h at RT, 2–6 h at 80°C). Incompatible with PU industry cycle times (seconds–minutes).	In situ NMR studies on aminolysis kinetics. Organocatalysts (TBD, DBU) tested for acceleration.	Catalysts improve rates but toxicity/scalability issues remain.	TRL 3–4 (lab scale)	Develop non-toxic, scalable catalysts; explore 6-membered cyclic carbonates for faster kinetics.
Hydroplasticization	Pendant –OH groups absorb water → Tg depression, mechanical weakening. No long-term outdoor durability data.	NIPU films with **clusteroluminescence** used to monitor humidity-driven softening in real time. Water-polymer interaction studies confirm Tg depression.	Hydroplasticization confirmed; sensing approach demonstrated.	TRL 3–4	Introduce hydrophobic segments, hybridize with epoxy/silicone, conduct systematic outdoor durability studies.
Molecular Weight Ceiling	NIPUs typically Mn = 15–25 kDa vs PU 40–80 kDa → weaker mechanical properties.	Catalyst-free synthesis with erythritol dicarbonate + long-chain diamines improved ordering. Transurethanization achieved Mn up to 95 kDa.	High MW achievable but energy-intensive; limited scalability.	TRL 4-5	Develop bio-based chain extenders, scalable post-polymerization strategies.
Biobased Diamine Availability	Most studies use petroleum-derived diamines (HMDA, IPDA, EDA). Bio-based diamines underexplored.	Diamines from dimerized fatty acids synthesized. Priamine (fatty acid-derived) used in NIPUs.	Bio-based diamines feasible but limited diversity.	TRL 3-4	Expand renewable diamine library (amino acids, lignin, algae).
LCA & Techno-Economics	Fragmented, lab-scale LCAs; no full cradle-to-grave comparison with PU.	LCA of biomass-derived PHUs/NIPTUs: min. selling price USD	NIPUs show sustainability potential but	TRL 4	Conduct standardized LCAs and techno-economic studies

		3.15–4.39/kg, reduced GHG emissions.	lack industrial benchmarks.		across full lifecycle.
Foaming Window Control	Poor control of gas release vs viscosity/gelation → inconsistent foam morphology.	Controlled epoxy functionality enabled rapid self-blown NIPU foaming. - Reviews highlight foaming inconsistencies.	Improved morphology possible but not systematic.	TRL3-4	Develop controlled foaming protocols, align with PU foam science.
Closed-Loop Recycling	Lab-scale recyclability demonstrated; industrial TRL low (3–4).	Bio-based NIPUs with dynamic covalent networks (CANs) showed self-healing and recyclability.	Recycling feasible at lab scale; industrial methods missing.	TRL 3–4	Scale CAN recycling to TRL 6; develop standardized industrial recycling pathways.
Six-Membered Cyclic Carbonates (6CCs)	Faster aminolysis kinetics but prone to homopolymerization; design rules missing.	6CC-based NIPU foams showed faster kinetics and improved mechanical properties. CO_2-derived 6CC networks exhibited recyclability.	High reactivity confirmed; stability challenges remain.	TRL 3	Establish design rules for 6CC stability vs reactivity; explore industrial synthesis routes.

Table 5. Research Gaps in NIPUs, Existing Studies, and Opportunities

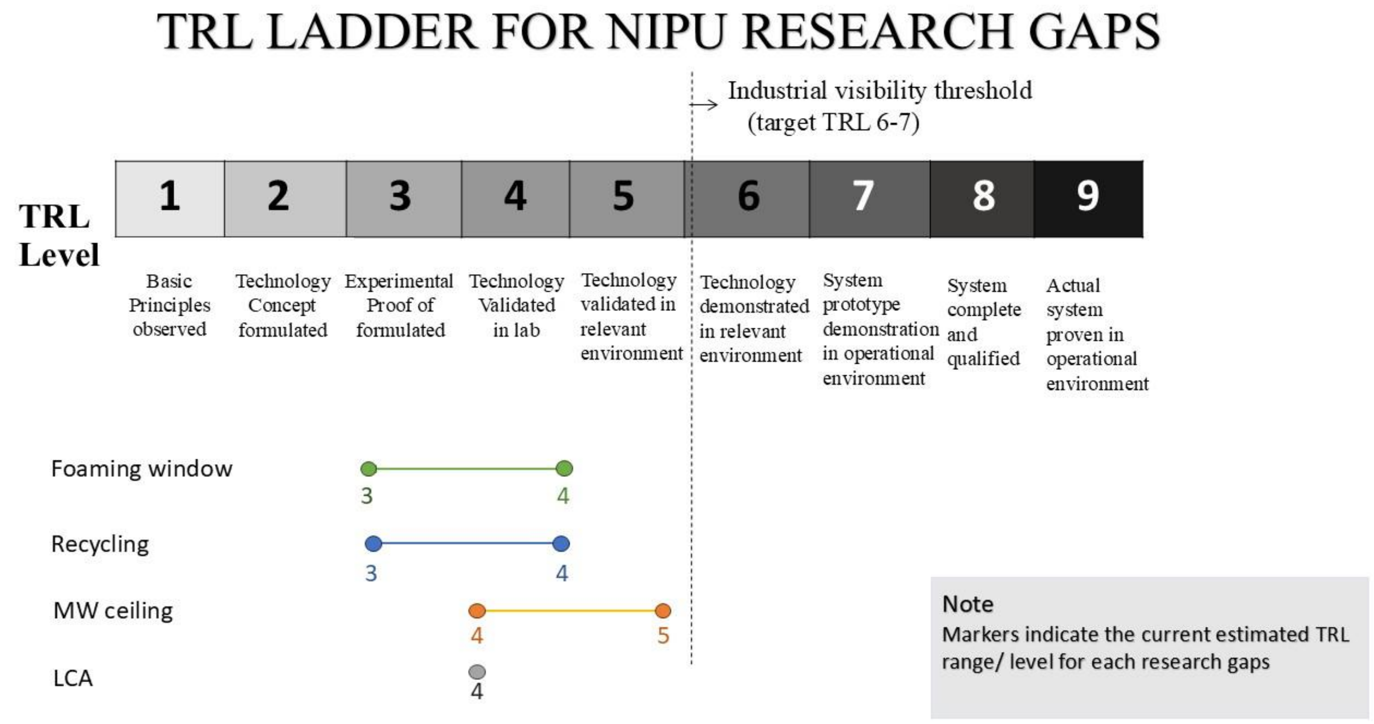


Fig 1. TRL ladder for NIPU research gap

6. Two crucial research gaps for industrial scalability

NIPUs are indeed a greener alternative for PUs, but their transition from a laboratory curiosity to a scalable industrial product requires overcoming two fundamental engineering bottlenecks: (i) Foaming Window Control and Poor Reproducibility; (ii) Closed-Loop Recycling without loss of performance.

6.1 Research Gap 1: Foaming Window Control in NIPU Foams

When water is added to isocyanates in conventional polyurethane foams, an in-situ reaction occurs that simultaneously creates urea linkages and releases CO_2. This procedure effectively synchronizes the blowing rate (gas generation) and the gelation rate (the construction of the polymer architecture to trap gas). This synchronization is seriously disturbed in self-blown NIPU foams. Five-membered cyclic carbonates (5CC) aminolysis is intrinsically slow, with slow reaction kinetics and poor regiocontrol. The gas either leaves too soon (producing flat, unfoamed resins) or expands after the matrix has already vitrified (causing cell collapse or splitting) since gas release frequently happens at a totally different pace or temperature than polymer cross-linking.

Key insights from the literature includes:

(i) Chaib et al. (2025, European Polymer Journal 229) where they addressed how chemical structures alter the foaming window. They mapped how aromatic vs. aliphatic epoxy functionalities alter activation energy (E_a). Aromatic systems show a significantly lower E_a. this promotes accelerating curing rates and rapid cell formation. On the contrary, aliphatic systems decrease the rate of reaction. They also determined a crucial industrial threshold and that is, if aliphatic content exceeds 30%, slow kinetics break the foaming window entirely, and this will to catastrophic foaming failure.

(ii) Singh et al. (2025, Polymer 333) reviewed foaming strategies such as **transurethanisation** and **thermal carbamate decarboxylation**. The study highlighted that while self-blowing NIPU foams are possible, the foaming window is narrow and highly sensitive to catalyst choice, blowing agent concentration, and curing temperature. Therefore, there is a high to need to explore catalyst engineering to widen the foaming window.

(iii) Earlier work by Detrembleur et al. (2015–2018) introduced the foundational principles of water-induced self-blown NIPU networks, demonstrating that carefully controlling water stoichiometry is vital to initiating foaming without fully decomposing the functional backbones. It required elevated temperatures (80–120 °C) and long synthesis times, limiting scalability.

(iv) **Xi et al. (2019)** ahowed rigid NIPU foams using **$NaHCO_3$ as a chemical blowing agent**. The process required heating to 200 °Cand also producing flammable byproducts and inconsistent foam morphology.

We can overcome the limitations highlighted in the above stidies by Molecular Design Strategies, Catalyst and Process Innovations and Engineering and Scale-Up Approaches.

(i) Molecular Design Strategies

However, Chaib showed that aromatic cyclic carbonates have reduced activation energy (35.72 kJ/mol) compared to aliphatic carbamates (58.35 kJ/mol). A rational approach would be to involve mixing of aromatic and aliphatic cyclic carbonates to utilize the advantage of fast curing (aromatic) and flexibility (aliphatic) of the product , while ensuring that the content of aliphatic remains under 30% threshold to avoid sluggish kinetics. Strategy of introducing electron-withdrawing substituents (e.g., phenyl ethers, halogens) near the carbonate ring can also be used. This will enhance electrophilicity and therby accelerating aminolysis. Temperature sensitivity reduces as the foaming window is widens up. Embedding reversible bonds (disulfide, imine, acetal) into the foam matrix allows stress relaxation during foaming, preventing collapse and enabling controlled expansion.

(ii) Catalyst and Process Innovations

Sensitivity towards selection of catalysts was brought up by Singh (2025). Strong organocatalysts like DBU, TBD, or ionic liquids help to reduce activation energy and accelerate aminolysis. Simultaneously, Dual-catalyst systems (e.g., TBAB + DBU) promote carbonate ring-opening and stabilize foaming kinetics. High temoerature levels (80–120 °C) were needed for the foaming process as deleveloped by Detrembleur. To overcome this, milder chemical blowing agents (e.g., bicarbonates, carbamate decarboxylation systems) that release CO_2 at lower temperatures, or bio-derived surfactants were used to stabilize cell morphology. Recent epoxy carbonate hybrid systems (Chaib, 2025) showed that partial epoxy conversion can trigger rapid exothermic curing. This generates heat internally and drive foaming without external high-temperature input.

(iii) Engineering and Scale-Up Approaches

Foaming of NIPUs is highly sensitive to viscosity changes and carbonate conversion rates. If the increase of viscosity occurs too rapidly, the bubbles will collapse before stabilization of the network. If the same happens too slowly foam drainage will take place and the structure will be lost. Here we must choose real-time monitoring through in situ rheology. This method will allow us to control the increase of viscosity and carbonate conversion rate and thus initiate foaming in an optimal manner.this method will avoid premature collapse. FTIR monitoring complements rheology by following the disappearance of carbonate peaks (around 1790 cm^{-1}) and the appearance of urethane carbonyl peaks (1700–1710 cm^{-1}). This gives a chemical fingerprint of conversion. These two methods together provide feedback control. By means of feedback control, adjustment of foaming initiation and ensurance of reproducibility can be done. Alternatively, it would be wise to increase the effictiveness of the procedure because continuous flow reactors with controlled CO_2 injection can maintain uniform reaction conditions therby widening the foaming window compared to batch processes. Hot spots and widening of the foaming window compared to batch systems can be prevented by flow reactors as they maintain laminar or turbulent regimes. Continuous processes are inherently more industrially viable as they allow foams to be produced with consistent density and morphology. This approach is similar to how petrochemical PU foams are already manufactured, but adapted to NIPU chemistry. Incorporation of Polysiloxane–polyether surfactants (as used in PU industry) can also be done. Siloxane segments anchor at the bubble interface while the polyether segments remain soluble in the polymer matrix and thereby increasing the effectiveness. This dual affinity stabilizes bubbles during growth. By tailoring surfactant molecular weight and hydrophilic–lipophilic balance (HLB), one can control cell size distribution, reduce coalescence, and minimize drainage. hydrogen bonding or ionic coordination can strengthen cell walls, making foams less sensitive to curing rate and temperature fluctuations. This will stabilize bubble growth, reducing sensitivity to curing rate and temperature.

6.2 Research Gap 2: Closed-Loop Recycling of NIPUs

Most current "recyclable" NIPUs utilize physical remolding (mechanical reprocessing) via Covalent Adaptable Networks (CANs) or vitrimers. However, physical hot-pressing under high temperatures for long durations triggers thermal degradation, bond breaking, and a steady decline in mechanical performance after only a few cycles. For true industrial scalability, we need closed-loop recycling. Chemically deconstructing a cured, cross-linked thermoset foam back into its initial building blocks (monomers or oligomers) at room temperature, purifying them, and re-polymerizing them into a virgin-grade material with 100% property retention.

Key insights from literature include:

(i) Miao et al. (2023) has developed an innovative bio-based NIPU network which is derived from carbon dioxide and lignin-derived feedstock. They introduced dual dynamic covalent bonds (transcarbamoylation + transacetalation). This features smart spiro bi-acetal structures. The network exhibits an activation energy of 70.34 kJ/mol. Additionally, they overcame the drawbacks of thermal hot-pressing by accomplishing total chemical breakdown at room temperature and then regenerating the material with almost 100% restoration of its original mechanical characteristics and structural integrity.

(ii) Thakur et al. (2024, European Polymer Journal 217) synthesized vanillyl alcohol-based NIPU vitrimers with cystamine, using disulfide bonds for chemical recycling. The NIPUs depolymerized via thiol–disulfide exchange in the presence of dithiothreitol (DTT). These reprocessed films retained 99.5% mechanical properties after multiple cycles.

(iii) Han et al. (2024, Polymers 16, 2277) developed a series of cross-linked bio-based Poly(hydroxyurethane-ureas (PHUUs) from renewable CO_2 and vanillin. They successfully engineered a closed-loop system by inserting a combination of reversible hydrogen bonds and dynamic imine networks. These systems degraded in 1M HCl/THF at room temperature and regenerated without altering chemical structure and achieved self-healing efficiencies above 95%.

43 (iv) Shermin et al. (2017) demonstrated fully bio-based poly(acetal) networks capable of water-mediated chemical recycling, restoring performance to its original state — a precursor concept now extended in NIPU systems.

We can overcome the limitations highlighted in the above stidies by Multi-Dynamic Bond Integration, Solvent-Free Recycling Protocols, Life-Cycle Assessment (LCA), and Pilot-Scale Validation

(i) Multi-Dynamic Bond Integration

One of the most promising strategies for closed-loop recycling is to design NIPU networks that contain multiple types of dynamic covalent bonds. Each bond reponds to a different stimulus like Disulfide bonds exchange under thiol triggers or moderate heat, Imine bonds hydrolyze under acidic conditions and reform upon neutralization, and Acetal bonds degrade in acid and regenerate under condensation conditions. By combining these chemistries in a single polymer backbone, the material can be recycled under different triggers (acid, thiol, heat) depending on the application or available recycling infrastructure. This "multi-trigger recyclability" ensures reliability: if one pathway is inefficient, another can be activated. It also allows selective recycling. For example, using mild acid for chemical depolymerization or heat for mechanical reprocessing.

(ii) Solvent-Free Recycling Protocols

Most current recycling demonstrations (Miao 2023, Thakur 2024, Han 2024) rely on solvents such as THF, DMF, or acidic aqueous mixtures. While effective in the lab, these approaches generate chemical waste and are impractical at scale. The next step is to design NIPU networks that can depolymerize under heat, humidity, or mechanical stress alone, without added solvents. For example incorporating reversible imine or acetal bonds that hydrolyze simply in moist air. If we engineer bond exchange reactions that can activate at moderate temperatures (60–100 °C), then this will enable hot-press recycling without solvents. Such solvent-free protocols would drastically reduce environmental impact and simplify industrial recycling processes.

57

(iii) Life-Cycle Assessment (LCA)

A life-cycle assessment is essential to prove that closed-loop NIPUs are not just chemically recyclable but also environmentally superior to conventional PU systems. It evaluates the entire journey of the material. Conventional PU disposal (landfill/incineration) generates significant CO_2 emissions and toxic byproducts. Closed-loop NIPUs, especially those derived from CO_2 and lignin/vanillin, can demonstrate a net reduction in greenhouse gas emissions by fixing CO_2 into polymers and enabling multiple reuse cycles. Traditional PU recycling often requires high-temperature pyrolysis (>300 °C). In contrast, NIPU systems (Miao 2023, Han 2024) achieve depolymerization at room temperature or mild heating (60–100 °C). LCA can quantify the energy saved per ton of recycled polymer and make a strong case for industrial adoption. LCA tracks how much of the original polymer mass and mechanical performance is retained after multiple recycling cycles. For example, Thakur (2024) reported 99.5% property retention after disulfide-based recycling. This efficiency directly translates into reduced raw material demand and lower environmental burden. By comparing NIPU recycling routes to conventional PU recycling/disposal, researchers can demonstrate the true sustainability advantage. This evidence is critical for convincing industry stakeholders, regulators, and policymakers to support NIPU adoption.

(iv) Pilot-Scale Validation

Most recycling demonstartions to date are lab scale, including small films, powders or test specimens. NIPUs must be scaled up to pilot scale to demonstrate its industrial vialbility. This wil help close the gap between academic proof of concept and industrial uptake. “Basically moving from grams to kilos. Pilot reactors need to demonstrate that acid- triggeed acetal degradation (Miao 2023), thiol–disulfide exchange (Thakur 2024), or imine hydrolysis (Han 2024) can be performed consistently at larger scales without loss of efficiency. Industrial foams and coatings need to be able to survive multiple rounds of recycling. Pilot studies should demonstrate at least 5–10 cycles with minimal property deterioration, proving that closed-loop recycling not just a one-time laboratory trick. Batch recycling inefficient for industry. Continuous flow reactors allow controlled depolymerization, purification, and re-polymerization in a single integrated process. This mirrors how petrochemical PU foams are already manufactured, but adapted to NIPU chemistry. Pilot-scale trials also assess whether recycling can be performed safely (no hazardous byproducts) and economically (energy and chemical costs lower than virgin production). This data is crucial for industry adoption.

7. Toxicology and Human Safety Profile

7.1 Elimination of Isocyanate Hazard

What's really good about NIPUs, health-wise, is clear: they completely get rid of dangerous isocyanate chemicals at every step—when making them, using them, and throughout their life. Regular chemicals like TDI, MDI, and HDI, which are called di- and polyisocyanates, can seriously irritate your lungs [51]. The EU's REACH rules even list them as "substances of very high concern," or SVHCs [52]. Breathing in even small amounts of this over time often causes occupational asthma, which is the most common lung problem people get from work in the EU [51] [53]. Once your body becomes sensitive to isocyanates, you can't reverse it. Plus, the phosgene gas used earlier in the process to make isocyanates is actually listed as a chemical warfare agent by the Chemical Weapons Convention [51].

On the other hand, no highly toxic chemicals are involved in the manufacturing step when NIPUs produced by adding CO2 to bio-epoxides and reacting them with amines. NIPUs not do react with other chemicals, do not cause allergic reactions and do not release any residual chemicals into the air during normal use when cured.

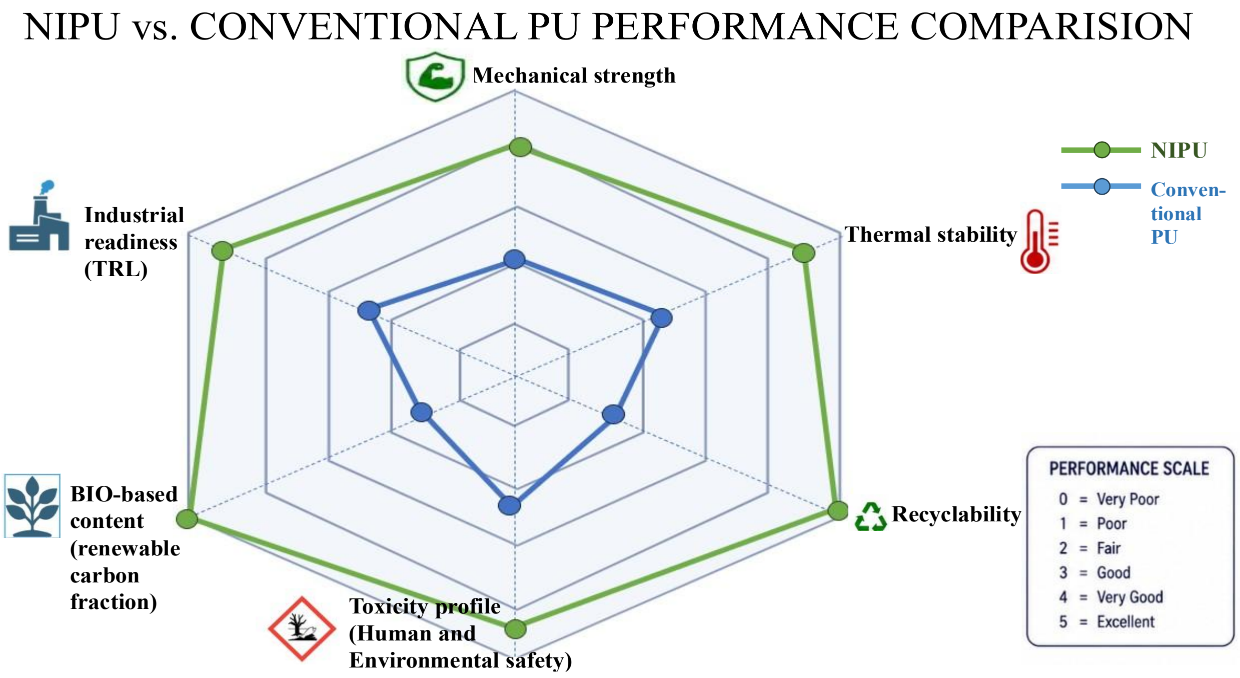
7.2 Biocompatibility and Cytotoxicity Data

When NIPUs are made with natural ingredients that are safe for the body, like CMC, gelatin, chitosan, or PEG, tests show that over 80% of cells (like mouse skin cells and human skin cells) stay alive. This means they pass the ISO 10993-5 standards for not being toxic to cells [54]. NIPUs changed with azetidinium are considered non-toxic to cells, and at the same time, they can kill bacteria, completely stopping E. coli and reducing S. aureus by almost 99% [43]. You can't get both of these benefits with regular PU systems [55].

There's one important exception: NIPUs that include Tea Tree Oil (TTO). In these cases, the essential oil changes the surface in a way that drops cell survival to about 46%. This shows that just because something comes from nature doesn't mean it's always safe for the body in every formula. So, it's still really important to test how toxic these materials are to cells at every step where they're modified.

7.3 Regulatory Status and Occupational Exposure

NIPUs aren't on the current list of "substances of very high concern" under REACH. This gives them a big leg up when it comes to rules and getting them into the market [2]. The amine parts of NIPUs that come from natural sources, like cadaverine and putrescine, are generally seen as safe in small amounts. You even find them naturally in fermented foods. Lab tests done so far suggest that the cyclic carbonate monomers used have low immediate toxicity. But we still need to do thorough safety studies, especially to check if the modified versions cause skin allergies [7].



8. Recyclability and Circular Economy Design

8.1 Recyclability and Circular Economy Design

Putting special changeable bonds into these NIPU materials lets us recycle them completely without making them weaker [39]. That’s a massive leap forward from the conventional approach towards dealing with such plastics after lifecycle. As the polyme is heated above its freezing point (T_v) all of the -OH groups adjacent to the urethane bonds begin the process. It consists of swapping th e amine portion of the one of the urethane bonds with on of the adjacent -OH groups. The process doesn’t destroy the polymer’s intergrity and the chemical bonds remain intact. However, it does make the arrangement of the material capable of flowing under stress, acting as a vitrimer during heating and pressuring [37], [56].

8.2 Foam-to-Film and Foam-to-Adhesive Conversion

Old NIPU foam items which are no longer in use are chopped and crushed. Then they are press with heat (around 5–15 MPa of pressure) at temperatures above T_v. Apart from activating the carbamate exchange, this process removes all the remaining cyclic carbonate in NIPU foam products, thus resulting in their complete liquification and further formation of solid plastic panels. These recycled materials are just as strong as new ones and can be used for structural panels, protective coatings, or even packaging [57]. If we're talking about NIPTU materials that contain disulfide bonds (made using cystamine-based crosslinkers), there's another clever trick: these disulfide bonds can also swap around, making them even easier to process again [16]. Adhesives made from recycled NIPTU can stick to glass and steel really well, up to 5.7 MPa. That's as good as some strong glues you can buy. Plus, they have a unique benefit: you can heat them to unstick them, then stick them back together just as well.

8.3 Chemical Recyclability via Hydrolysis and Aminolysis

If you use controlled alkaline hydrolysis, NIPU materials can be chemically broken down all the way back to their original building blocks, the diamine and diol. This is true chemical recycling, where you get the monomers back, similar to how PET plastic can be recycled through glycolysis [58]. Currently there is no best way that has been figured out to do this chemical breakdown on a large factory scale in terms of energy and chemicals. But this method is what we're aiming for to create a truly circular economy for NIPU materials [59].

Application sector	**NIPU System**	**Key Properties**	**Typical uses**	**References**
Thermal insulation foams	Tannic acid / chitosan + $scCO_2$ blowing	Flame retardancy, low density	Building insulation	[22], [60]
Anti-corrosion coatings	Epoxy–NIPU hybrids	Strong adhesion, barrier protection	Steel, aluminum, wood	[7], [61]
Structural adhesives	Cyclic carbonate + amine curing	High shear strength, low emissions	Furniture, engineered wood	[11]
Flexible cushioning foams	PMHS/amine or azodicarbonamide/ZnO blowing	Uniform cell structure, resilience	Automotive seats, mattresses	[6], [22]
Biomedical materials	Functionalized NIPUs with azetidinium	High WVTR, antibacterial, cytocompatible	Wound dressings	[43], [44]
UV-curable coatings	Hydroxyurethane methacrylate (HUMA)	Rapid curing, safe chemistry	Dental restoratives, 3D printing	[54]
Smart/self-cleaning coatings	PDMS-NIPU copolymers	Ultra-low surface energy, self-healing	Protective coatings	[46]
Aerospace/marine coatings	Amino-telechelic NIPU/epoxy	Impact/salt-spray resistance, thermal stability	Aircraft, ship hulls	[9]

9. Industrial Applications

NIPUs have unique combination of isocyanate-free synthesis, tunable mechanical properties, excellent interfacial adhesion, and recyclability. This allows NIPU to serve across diverse industrial sectors. Table 6 summerizes these applications:

Table 6. Industrial Application landscape for NIPU materials

8.2 NIPU Composites with Natural Fibers

NIPUs combine well with natural fibers such as jute, flax, hemp, and bamboo to form biocomposites that are lightweight, renewable, and biodegradable [62]. These fibers have densities around 1.3–1.5 g/cm^3, much lower than glass fiber (≈ 2.5 g/cm^3), yet they provide comparable strength and stiffness [63].

Fiber–matrix adhesion is a key advantage of NIPUs. The PHU backbone contains many –OH groups that bond strongly with hydroxyl and carboxyl groups on cellulose and lignin in the fiber. This creates hydrogen bonds and ester linkages, improving stress transfer between fiber and matrix [62]. Under mild heat, these –OH groups can form covalent bonds with the fiber surface, giving better mechanical integrity than conventional PU composites [62]. The three main fabrication routes used are: (i) Hand lay-up with pre-impregnated NIPU resin. It is good for complex shapes but limited to atmospheric curing [64], (ii) Resin transfer molding (RTM) using low-viscosity NIPU prepolymers. This helps in achieving high fiber content (30–50 vol %) but requires careful viscosity control during curing [65], [66], (iii) Bio-composite pressing where there is mixing of chopped fibers with cyclic carbonate and amine, then hot-pressing at 120–150 °C for 30–60 min to make structural panels and packaging materials [4].

A major challenge is fiber moisture management. Natural fibers contain 6–12 wt % bound water. Although this moisture doesn’t react with NIPU chemistry (unlike isocyanates). It can cause dimensional instability under humidity cycles. Pre-drying fibers below 2 wt % moisture and applying hydrophobic surface treatments (silane or epoxy) can reduce this instability by up to 80 % [70] .

Fibre Type	Density (g/cm³)	Tensile Strength (GPa)	Elastic Modulus (GPa)	NIPU Matrix Used	Composite Property Highlights	Development Status	Refrences
Jute	1.3-1.46	0.2-0.8	10-30	Carbonated soybean oil/ HMDA	Flexural strength 85-120MPa Good moisture resistance after silane surface treatment; inherently fire-retardant composite when tannin co-filler added	Lab scale; few peer-reviewed Studies; significant optimization needed	[9], [62]
Flax	1.4-1.5	0.5-1.5	27.6-80	Carbonated linseed oil/ IPDA	High specific stiffness (modulus 20–35 GPa for unidirectional); excellent NIPU–flax affinity due to –OH surface compatibility; low void content	Lab scale; promising LCA profile; moisture uptake remains challenge	[63]
Hemp	1.48	0.55-0.9	70	Carbonated sunflower oil/ EDA	High aspect-ratio fibers; good impact energy absorption; waxy surface requires alkali or enzyme pretreatment to improve NIPU adhesion	Emerging; limited NIPU-specific data; hemp-epoxy data more abundant	[65], [68]
Sisal	1.33-1.5	0.47-0.7	9-22	Bio-based PHU (glycerol carbonate-based)	Medium stiffness; good dimensional stability; alkali treatment increases NIPU–fiber bond	Exploratory stage; data from conventional PU composites used as proxy	[69], [70]

					strength by 40–60 %		
Bamboo	0.6-1.1	0.14-0.8	11-17	Carbonated castor oil / cadaverine	Lightweight; fast renewability (3–5 year harvest cycle); natural antibacterial; NIPU matrix compatible with bamboo lignin surface chemistry	Very early stage for NIPU; conventional PU bamboo composites well-studied	[34]

Table 7. NIPU natural fibre composites

9. Novel Conceptual Contributions

9.1 The Reactive CO_2 Dual-Function Platform

There are three roles CO_2 plays. The core is the Reactive CO_2 Dual-Function (RCDF) Platform. Taking an amine-functionalized bio-based precursor something like fatty acid diamine-modified epoxidized soybean oil and exposing it to CO_2 at moderate temperature and pressure is the basic step. At that point, three things happen at once. No separate monomer synthesis step as the CO_2 reacts with epoxide groups to form cyclic carbonate monomers on the spot [71]. Dissolved CO_2 also forms carbamate salt intermediates with the amine groups. When the pressure is released and the temperature is ramped, the carbamate salts decompose releasing CO_2 that blows the foam while simultaneously driving network crosslinking [12].

The foam network is a covalent adaptable network from the beginning because it formed from carbaate and carbonate exchange chemistry. This the same chemistry that made the material also makes it recyclable [37].

The practical implications are significant. A one-pot architecture like this could remove te need for separate monomer synthesis reactors, cut out external blowing agent supply chains, and remove the post-synthesis steps currently needed to introduce CAN behavior [72]. That's not a minor tweak it's the kind of simplification that could genuinely shift the economics of NIPU foam production.

9.2 Bifunctional Lignin-Carbonate Macromonomers as Reactive Dispersants in WNIPUs

Material that comes in discussios of sustainability without ever quite fulfilling its potential is lignin. It's the most abundant aromatic biopolymer on the planet but still in most current NIPU formulations it's used passively as a filler or a crosslinker [73].

There is a need to engineer lignin as a bifunctional reactive dispersant in waterborne NIPU systems. The idea can be exceuted by partially carbonate the phenolic hydroxyl groups on lignin to create reactive cyclic carbonate sites for aminolysis crosslinking, while modifying the remaining free phenolics with sulfonate groups to give the molecule anionic self-emulsifying character [74].

Replacing both the reactive monomer fraction and the surfactant component in a single material means fewer components, fewer synthesis steps, and a simpler, cheaper formulation. For waterborne NIPU adhesives and coatings where cost and complexity are real barriers to adoption that kind of consolidation could matter a lot [43], [75].

9.3 NIPU-Based Bioadhesive Hydrogels for Wound Closure

This one is in an intersection that no oone seems to have quite explored yet. A bioadhesive hydrogel platform with a genuinely unusual combination of properties can be produced by combining a cytocompatible bio-based PHU backbone with CMC or alginate modifiers, azetidinium antimicrobial crosslinks, and hydrophilic PEG segments [75]. It would provide antibacterial action through the azetidinium groups [44]. Controlled moisture vapor transmission important for wound healing environments would be given by the PEG and CMC components [76]. Degradation would produce bio-based fatty acid diols and diamines and these are non-cytotoxic. Simply by adjusting crosslink density through the PEGDA ratio stiffness could be tuned, which means the same platform could potentially be adapted for different tissue types rather than being locked into a single application [49].

The most important thing about this concept is that it do not have isocyanates. Isocyanate toxicity has been the biggest obstacle blocking polyurethane-based materials from approval in wound-contact and implantable applications for decades [51]. An NIPU-based system removes that barrier entirely. It helps in opening up regulatory doors that conventional PU chemistry simply cannot access. This describes a formulation space that has not been explored as a cohesive platform and that gap is indeed an opportunity to do further advancements.

10. Conclusion

This thesis demonstrated a transformative class of polymers that's is NIPU. This class is capable of addressing the toxicological, environmental and regulatory challeneges associated with conventional isocyanante-based

PUs. Systematic review of fundamental synthetic routes like cyclic aminolysis, transurethanization, ring-opening polymerization, and CO_2 based monomer synthesis is done. Therefore, highlighting both the mechanistic diversity and the atom economical efficiency that make NIPUs uniquely suited for green chemistry and circular economy integration. Current advancements in hybrid structures (epoxy/NIPU blends, hydroxy urethane methacrylates, thiourethane systems), waterborne dispersions, and UV-curable resins have increased the performance of NIPUs and now are used in wide range of applications like coatings, adhesives, foams, and biomedical materials. Two critical industrial bottlenecks which are foaming window controland closed-loop recycling are explained in the thesis. These are the key hurdles which must be overcome for large-scale production. Strategies to bridge the gap are proposed like aromatic-aliphatic cyclic carbonate balancing, catalyst engineering, multi-dynamic bond integration and solvent-free recycling protocols. Further, emphasis has been done on the importance of toxicology and regulatory compliance, showing how NIPUs align with REACH directives and occupational safety standards. This thesis also discusses opportunities for the production of biocomposites using natural fibres such as jute, flax, hemp and bamboo. Besides being low density and sustainable materials , these composites also have good interfacial adhesion because of the abundance of hydroxyl groups on the NIPU backbone. Finally three innovative ideas that is the RDCF platform, bifunctional carbonate macromonomers based on lignin, and bioadhesive hydrogels made of NIPUs are introduced to facilitate the transition of NIPUs from lab scale to industrial scale use. All these achievements make the introduction of NIPUs as a realistic an environmentally friendly polymer technology more plausible than ever before. This thesis proposes NIPUs not just as another polymer but as the polymer of the next generation. It combines carbon capture and utilization, sustainable chemistry, recycling and performance features, therefore opening the way for NIPU application in a wide range of areas.

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