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Non-isocyanate polyurethane from bio-based feedstocks and their interface applications

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Non-isocyanate polyurethane (NIPU) has emerged as a promising material to substitute conventional polyurethane (PU) that relies on toxic precursors—*isocyanates*. Aligned with the principles of green chemistry, environmental friendliness, and sustainability, NIPU from bio-based materials has gained significant interest in recent years. This review aims to provide a comprehensive overview of NIPU synthesis methods and their various classifications. It also highlights bio-based precursors in NIPU synthesis, supported by detailed case studies. Furthermore, the review explores the potential application of bio-based NIPU at interfaces such as coating, adhesive, and biomedical materials. Finally, the current limitations and perspectives on the development of bio-based NIPU are discussed.

1. Introduction

Since its discovery by Otto Bayer in 1937, polyurethane (PU) has become a major component of polymer production.¹ Benefiting from versatile properties such as elasticity, toughness, and chemical resistance, PU is widely used in coatings, foams, sealants, and adhesives.^{2–6} Nowadays, PU occupies a significant market share, with a world market value exceeding \$65 billion, and this value continues to grow.⁷

As shown in Fig. 1, PU is generally synthesized *via* the polyaddition between diols/polyols and diisocyanates/polyisocyanates. Polyols, with their long chains, impart flexibility to the final product and serve as the soft segment,

whereas polyisocyanates form the hard segment due to their rigidity. Consequently, the resulting PU combines both flexibility and hardness. The properties of PUs can be tailored by selecting different types of polyisocyanates and polyols.^{8,9} However, as a primary raw material, isocyanates are industrially derived from toxic phosgene gas, and exposure to isocyanates can lead to severe health issues, including asthma.¹⁰ Additionally, the reaction between isocyanates and water generates CO₂ and amines, which can influence the final properties of PU, particularly in coatings. Therefore, the production, transportation, and storage of PU require stringent safety measures.

With growing concerns about environmental protection and the safety of production and consumer goods, NIPU has garnered much attention in both academia and industry. First introduced by Dyer and Scott in 1957, NIPU offers advantages such as the absence of moisture-sensitive and

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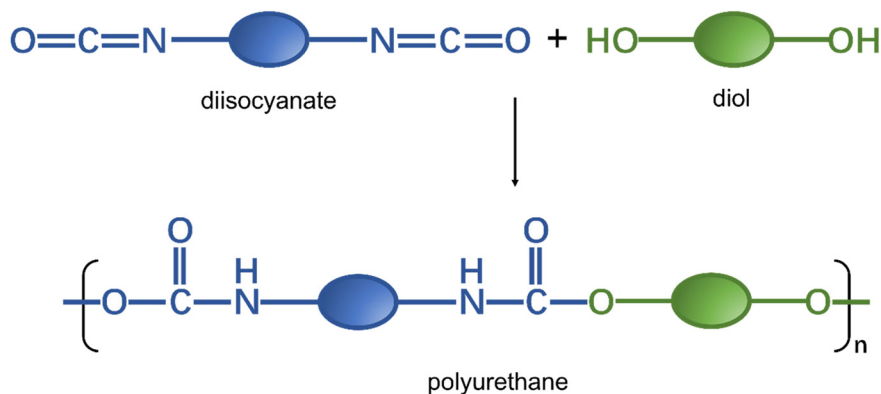


Fig. 1 Polyaddition reaction of diisocyanate and diol to generate polyurethane.

toxic isocyanates, positioning it as a promising alternative to conventional PU.¹¹ In addition, the scarcity of petroleum-based feedstocks, combined with a heightened focus on green chemistry and sustainability, has driven efforts to

develop NIPU from bio-based resources. In recent years, numerous studies have explored bio-based NIPU, demonstrating its potential applications.^{12–14}

In this review, we will first introduce the various synthetic pathways for NIPU and examine different bio-based precursors employed in NIPU synthesis. Finally, we will summarize potential interface applications of NIPU, highlighting recent advancements in the field.



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2. NIPU synthesis routes

The conventional synthesis of PU relies on the reaction between diisocyanates and polyols to form urethane linkages. Among various available diisocyanates, toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) are the most widely used in industrial production.¹⁵ In recent years, the drive for environmental protection and the implementation of green chemistry principles have led to the emergence of NIPU as an alternative to traditional PU. This shift is largely motivated by stringent regulations on volatile organic compounds (VOCs) and the potential hazards of isocyanates. Several comprehensive reviews have been published recently, as shown in Fig. 2,



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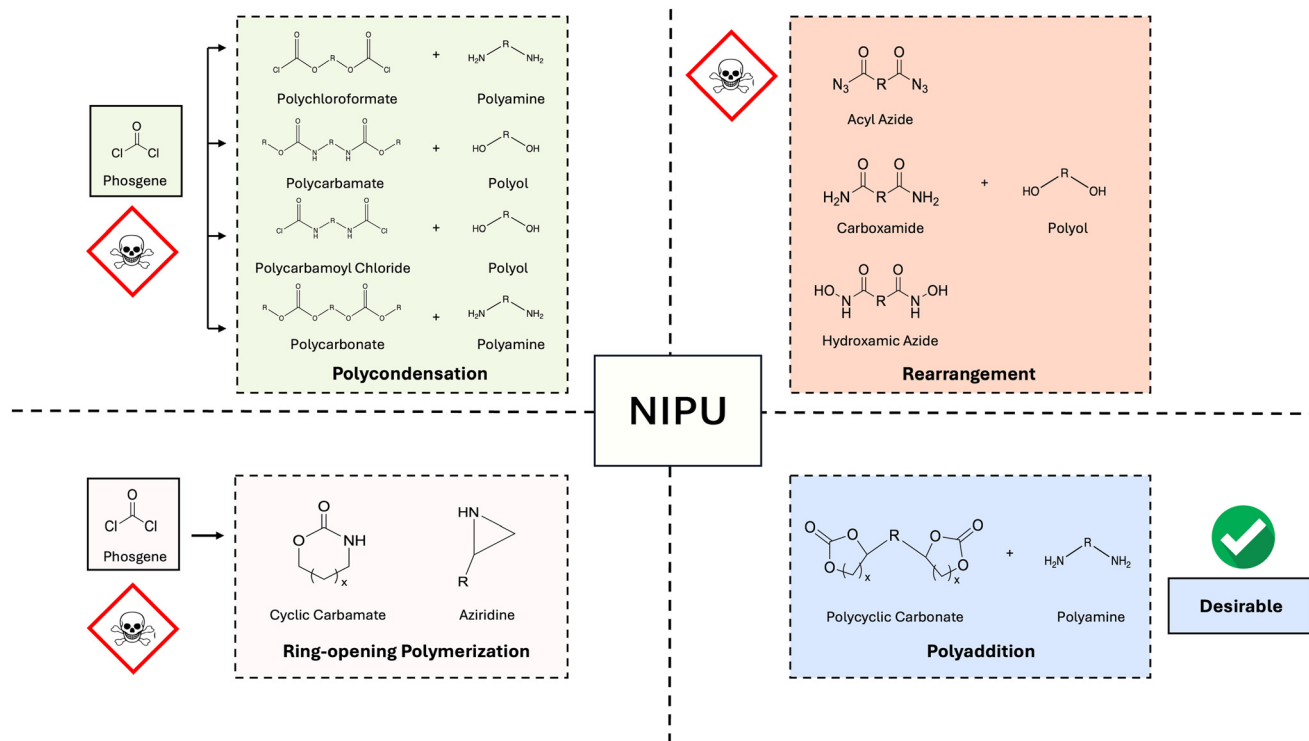


Fig. 2 Non-isocyanate methods for NIPU synthesis.

providing a thorough overview of the various methods for synthesizing NIPU and highlighting the significant progress in this rapidly evolving field.^{16–20}

2.1 Polycondensation

Polycondensation is one of the conventional routes for NIPU synthesis, involving the reaction between various precursors, such as polychloroformate and polyamine, polycarbamate and polyol, polycarbamoyl chloride and polyol, or polycarbonate and polyamine. Despite the diversity of polycondensation routes, they still face several challenges that have hindered their industrial application.^{21,22} One of the primary limitations is the reliance on phosgene or its derivatives for the synthesis of precursors, which are highly toxic and hazardous chemicals. Additionally, side-products such as HCl and alcohols are released during polycondensation reactions, which can be problematic for large-scale production and require additional processing steps for their removal. Furthermore, this reaction often requires high temperatures or catalysts to achieve satisfactory reaction rates and polymer molecular weights, adding to the complexity and cost of the process.

Recent advancements have shown promise in addressing these challenges. Wołosz, *et al.* developed an innovative approach using dimethyl carbonate, a green and eco-friendly substitute for phosgene, along with diamines to synthesize alkylene and arylene bis(methyl carbamate)s.²³ Although dimethyl carbonate (DMC) eliminates chlorine-bearing reagents, the process still needs elevated temperatures (~120 °C) to strip methanol and a recycling loop for excess DMC, limiting scale-

up.²⁴ Likewise, a one-pot lignin-based NIPU adhesive prepared *via* DMC-mediated trans-urethanization cuts halogen waste but still operates above 110 °C.²⁵ In short, the extra heat and solvent-recycling steps keep polycondensation at the pilot stage.

2.2 Rearrangement

The synthesis of NIPUs *via* rearrangement reactions offers an alternative approach. This approach involves the use of acyl azides, carboxamides, or hydroxamic azides, which undergo various rearrangements to form a key intermediate, including Curtius rearrangement, Hoffman rearrangement, and Lossen rearrangement.^{26–30} Recent studies have translated these reactions into continuous-flow microreactors, greatly shortening residence times and better containing energetic azides.³¹ Mallia *et al.* further demonstrated kilogram-scale Curtius rearrangements under flow, underscoring the potential for scale-up.³² Even so, the need for explosive azide precursors and the high-temperature evolution of N₂/CO₂ demand stringent safety controls and have confined this chemistry to gram- or pilot-scale demonstrations. In short, the use of highly hazardous reactants, such as azides, remains the main obstacle to wide industrial adoption.

2.3 Ring-opening polymerization

The third approach to synthesizing NIPUs involves the ring-opening polymerization (ROP) of aliphatic cyclic carbamates or aziridines.^{33–36} This method is attractive because it generates no small molecule by-products, making purification easier. However, several limitations have restricted its broader



application. Most cyclic carbamates are still synthesized from phosgene-derived chloroformates, reintroducing toxicity concerns. When aziridines are used as monomers, additional safety risks arise due to their acute toxicity and sensitization potential.³⁷ Moreover, this polymerization typically requires high reaction temperatures—often above 140 °C—to achieve sufficient molecular weight, leading to high energy consumption and limited substrate compatibility. Although some recent catalysts have reduced the required temperature to around 110 °C, the trade-off is often slow reaction or broader molecular weight distributions.³⁸ As a result, ROP-based NIPUs are mainly explored in specific areas such as adhesives and foams, rather than in large-scale or structural applications.³⁹

2.4 Polyaddition

Because the preceding three routes each carry safety or performance issues, research has steadily pivoted toward the polyaddition of cyclic carbonates (CCs) with amines. This method eliminates the need for toxic isocyanates or phosgene as precursors, making the entire process safer, more environmentally sustainable, and better suited for a broader range of applications. For example, Cornille, *et al.* first reported the synthesis of PU foams from the reaction between cyclic carbonates and diamine to yield NIPU foams in 2015. These synthesized high-density flexible NIPU foams (194–295 kg m⁻³) exhibit excellent thermal stability and recoverable compression behavior.⁴⁰

In the polyaddition, the amine, acting as a nucleophile, attacks the carbonyl carbon of the cyclic carbonate (five-membered or six-membered ring), followed by a proton transfer step that results in the formation of a primary or secondary hydroxyl group. Due to the presence of hydroxyl groups attached to the main polymer chain, the final products of this method are termed poly(hydroxyurethane)s (PHUs). The hydroxyl groups enhance the material's unique properties by promoting hydrogen bonding, which improves chemical resistance to non-polar solvents. Additionally, this synthesis route offers significant flexibility in terms of raw materials, allowing for the use of a wide range of cyclic carbonates and amines derived from biodegradable, renewable, and sustainable resources as bio-based precursors.

The structures of both amines and CCs significantly influence the polyaddition reaction. Primary aliphatic amines, attached to a primary carbon with electron-withdrawing groups at the α or β position, are generally more reactive than secondary or aromatic amines.⁴¹ As for CCs, the reactivity order follows CC5 < CC6 < CC7 < CC8, with larger ring sizes exhibiting higher reactivity due to greater strain energy.⁴² Despite its lower reactivity, CC5 has been the focus of extensive research, primarily because the synthesis of more reactive cyclic carbonates (CC6, CC7, and CC8) often requires harmful precursors, including phosgene or its derivatives, which again raises significant safety and environmental concerns.⁴³ Solvent, temperature, and catalysts further steer the rate and molecular weight of poly(hydroxyurethane)s (PHUs).^{44,45}

Even with such tuning, PHU resins face three practical hurdles: high viscosity, slow room-temperature cure, and ever-stricter VOC limits. Rather than invent new chemistries, researchers now tackle these issues at the formulation level. The next two subsections highlight the main fixes: waterborne NIPU dispersions that decrease viscosity and VOCs, and hybrid NIPU networks that co-crosslink PHU segments with fast reactants of epoxy, acrylate, or siloxane to speed cure and boost film performance.

3. Specialized NIPUs: waterborne and hybrid systems

3.1 Waterborne non-isocyanate polyurethane (WNIPU)

The development of waterborne non-isocyanate polyurethanes (WNIPUs) offers an eco-friendly alternative to conventional solvent-based polyurethane chemistry. Water, as a green dispersing medium, not only addresses environmental concerns but also introduces unique challenges in PU design and synthesis. The key to successful WNIPU development lies in achieving stable aqueous colloidal dispersions while maintaining the desirable properties. Based on the stabilization mechanisms in aqueous media, WNIPUs can be classified into three distinct categories: cationic WNIPUs, anionic WNIPUs, and nonionic WNIPUs. Each type of unique molecular design strategy not only affects the stability of the dispersion but also influences the final properties of the polyurethane films, such as water resistance, adhesion, and mechanical strength.⁴⁶ In this section, an overview of the different types of WNIPUs and the primary dispersing methods in their preparation will be discussed.

3.1.1 Types of WNIPU

3.1.1.1 Cationic WNIPUs. Cationic WNIPUs are synthesized through a well-defined three-step process—prepolymer synthesis, neutralization, and emulsification, as shown in Fig. 3. In the prepolymer synthesis step, cyclic carbonate reacts with amine-containing tertiary amine groups, such as *N*-methyl diethanolamine (NMDEA) or 3-dimethylaminopropane-1,2-diol (DMAD), resulting in a prepolymer. Subsequently, the prepolymer undergoes neutralization using a neutralizer, such as acetic acid⁴⁷ or carboxylic acid.⁴⁸ Finally, deionized (DI) water is added for emulsification to obtain cationic WNIPU dispersion. Based on the summary of ionic type in Table 1, the cationic WNIPUs gained more interest. In 2018, Ma, *et al.* developed WNIPU with polyamines as internal dispersing agents, which were neutralized by carboxylic acid. The corresponding polyurethane coatings had a film thickness of about 30 μm and promising material properties such as good impact and solvent resistance.⁴⁹ The same year, Ma, *et al.* developed another WNIPU of high molecular weight from *N*-*N'*-di-*t*-butyloxycarbonyl isophorone diamine (DiBoc-IPDC) and diols/diamines using alkali bases as catalysts. The corresponding PU coating also exhibited satisfactory impact and solvent resistance.⁵⁰ In 2020, Zhang, *et al.* first published cationic WNIPU epoxy hybrid coatings prepared from waterborne amine-terminated NIPU and waterborne epoxy





Fig. 3 The general synthesis steps for cationic, anionic, and nonionic WNIPU.

Table 1 Summary of waterborne NIPU coatings in recent studies

Cyclic carbonate	Amine	Emulsifier	Neutralizer	Cure temp °C	Type ^a	Ref.
BDMC; CHBMC; IPDMC	PPGda230; TOTDDA	EDTAD; CHTCD	TEA	50, 110–150	A	53
DiBoc-IPDC	PPGda; PPG; TOTDDA; TEG	DMDPA	Acetic acid	50	C	50
BMDC; IPDMC	PPGda400; PPGda230; DMHD; pTHFda1100; TOTDDA	DETA; BAPA; DMDPA	Carboxylic acid	130	C	49
DGC; (bis)N-8-C	PDMS-diamine	(bis)N-8-C	Carboxylic acid	80	C	48
Sorbitol-based CC	HMDA/IPDA	Anhydrides	TEA	120	A	54
Dimethyl carbonate	FDA	DMDPA	Acetic acid	100	C	51
Linseed oil cyclic carbonate	FDA	DMDPA	Acetic acid	120	C	52
Carbonated linseed oil	HDA; <i>m</i> -XDA; EDR	DMDPA	TEA; acetic acid	78	A; C; N	47
Di- <i>tert</i> -butyl dicarbonate	FDA	Tertiary amine	DL-lactic acid	130	C	55

^a Ionic center type (A = anionic; C = cationic; N = non-ionic).

chain extender. This method accelerated the curing process of the NIPU by employing epoxy as a bridge. The waterborne amine-terminated NIPU was derived from diglycerol dicarbonate, fatty acid diamine (FDA), and 3,3'-diamino-*N*-methylpropylamine (DMDPA) as an internal dispersion agent, which was neutralized by acetic acid. The waterborne epoxy chain extender was synthesized from diethanolamine and trimethylolpropane triglycidyl ether (TTE).⁵¹ In 2023, Ling, *et al.* developed waterborne NIPU coatings using biobased and eco-friendly linseed oil. A linseed oil was modified through thiol-ene reaction and esterification, resulting in cyclic carbonate.⁵² Then the linseed oil-based cyclic carbonate reacted with a bio-based fatty acid diamine and an internal dispersion agent to generate WNIPU.

3.1.1.2 Anionic WNIPUs. The synthesis of anionic WNIPU includes an additional step between prepolymer synthesis and neutralization known as anhydride modification, as shown in Fig. 3. The amine-terminated prepolymer is modified by anhydride, such as ethylenediaminetetraacetic dianhydride (EDTAD), succinic anhydride, maleic anhydride, and *o*-phthalic anhydride, to obtain a carboxyl-terminated polymer. Then, it is neutralized by an alkaline neutralizer, such as triethylamine (TEA). Finally, DI water is added for emulsification to obtain anionic WNIPU dispersion. However, this synthesis is not

suitable for preparing high molecular weight PU resins because the concentration of dispersing ionic groups would be too low to stabilize the polymers in an aqueous medium. Ma, *et al.* developed an anionic WNIPU dispersion with diamines, dicarbamates, and dianhydrides as monomers. The corresponding coatings cured at elevated temperatures exhibited much better material properties than those cured at 50 °C.⁵³ Wu, *et al.* reported sorbitol-based anionic WNIPU. The sorbitol-based cyclic carbonate was reacted with different anhydrides to introduce carboxyl groups. After that, the carboxyl groups were neutralized by TEA and dispersed in water to synthesize aqueous cyclic carbonate dispersions. The WNIPU coatings exhibited excellent flexibility, adhesion, gloss, and impact resistance as well as good thermal stability when the molar ratios of isophorone diamine (IPDA)/hexamethylene diamine (HMDA) ranged from 1:1 to 1:3.⁵⁴ In 2024, Pichon, *et al.* developed cationic waterborne and bio-based non-isocyanate poly(urethane)-urea dispersions for coating applications neutralized with lactic acid.⁵⁶

3.1.1.3 Non-ionic WNIPUs. The synthesis of non-ionic WNIPU involves a slightly different approach with three main steps: grafting modification, prepolymer synthesis, and emulsification. In the first step, hydrophilic segments are introduced into the cyclic carbonate using polyols or diols, such as polyethylene



glycol (PEG) or its derivatives, to enhance water solubility. The modified cyclic carbonate is then reacted with amine chain extenders to form the non-ionic WNIPU prepolymer. Finally, the prepolymer is dispersed in DI water to form a stable non-ionic WNIPU emulsion. Zhang, *et al.* developed a non-ionic WNIPU through the grafting modification of amine-polyethylene glycol-monomethyl ether (mPEG-NH₂) to provide water solubility. The corresponding coatings exhibited tailorable cloud points ranging from 60 to 80 °C.⁴⁷

3.1.2 Dispersing method. The first example of a NIPU water-based dispersion was reported by Blank, *et al.* in 1996.⁵⁷ They synthesized cross-linked polyurethanes using a transurethanization process with polyester polyols, bis-hydroxypropylcarbamates, and triol.⁵⁸ This pioneering work established the foundation for the further development of WNIPU systems. Several methods have been developed to prepare stable WNIPU dispersions: (1) prepolymer mixing process, (2) acetone process, (3) melt dispersion process, and (4) ketamine/ketazine process.⁵⁹ Among these, the prepolymer mixing process and the acetone process are widely utilized for their efficiency and versatility. In the prepolymer mixing process, the initial reactive prepolymer is first synthesized and then neutralized to form ionic groups. Finally, the neutralized prepolymer is dispersed in water under controlled conditions to form a stable aqueous dispersion. The success of this process relies heavily on prepolymer design, particularly the incorporation of sufficient hydrophilic segments and optimal neutralization of ionic groups. This solvent-free approach simplifies processing steps and eliminates concerns associated with organic solvent removal. The acetone process employs a solvent-mediated approach for WNIPU synthesis, where the prepolymers are first synthesized in acetone or other low-boiling-point solvents. Following synthesis, the solution is dispersed in water, followed by acetone removal. The use of acetone as a reaction medium provides better control over molecular weight and prevents hydrolysis. These established dispersion methods have laid a solid foundation for WNIPU development, enabling the preparation of stable aqueous dispersions with controlled properties.

3.1.3 Current limitations of WNIPU. Recent literature confirms that the key drawbacks of WNIPUs remain (1) limited molar mass and (2) intrinsically sluggish aminolysis kinetics. Comprehensive reviews of the field show that most five-membered-cyclic-carbonate/amine systems plateau at number-average molecular weights of *ca.* 20 kDa, well below the 40–80 kDa typically reached by commercial waterborne polyurethanes based on isocyanates.^{60,61} Even when fatty-acid-derived chain extenders are used to boost chain length, the number-average molecular weight typically reaches only 30–33 kDa. This suggests that, although chain extension promotes additional chain growth, it does not fundamentally overcome the intrinsic limitations of the system.⁶² Also, the reported broad dispersity of the waterborne polyurethane ($D \approx 2.5\text{--}3.1$) is attributed to the reduced mechanical performance.

Low conversion rates exacerbate the problem. A kinetic analysis of the aminolysis of carbonated methyl-oleate shows that the second-order rate constants are one to two orders of magnitude below those in isocyanate chemistry; therefore, significant conversion requires either >100 °C reaction temperature or extended reaction time.⁶³ In practical coating recipes, it usually requires four days for solvent- and catalyst-free WNIPU synthesis to reach acceptable conversion at 75 °C, delivering pre-polymers that again stall at ~20 kDa.⁶⁰ Although strategies such as β -hydroxylamine accelerators or epoxy chain extenders solve the issue, they involve additional reactive steps rather than fundamentally speeding up the urethane-forming reaction. Therefore, to overcome the limitations of low molecular weight and slow curing, it remains essential to explore one-pot chain extension-dispersion processes or develop more reactive multifunctional carbonates.

3.2 Hybrid NIPU

By hybridization with different materials, such as epoxy resins, unsaturated compounds, and siloxanes, it overcomes the shortcomings of traditional NIPU in terms of low molecular weight and poor mechanical properties and achieves diversification and comprehensive performance improvement.^{64,65} Compared to single-type NIPU, the multifunctionality of hybrid NIPU comes from the synergy between different groups. For example, the high toughness of epoxy resin complements the flexibility of NIPU to increase its mechanical properties. Through the introduction of unsaturated acrylates, the hybrid NIPU has excellent weather resistance and photopolymerization capability, further expanding its potential in high-performance coatings.⁶⁶ The introduction of siloxane or bio-based materials enables NIPU to have new applications in specific functional fields, such as medical materials, environmental protection coatings, *etc.* The variety of NIPU hybridization methods is based on the design of different reaction paths and combinations between cyclic carbonates, hybrid groups, and amines. This strategy needs to consider material properties, processing technology, and synergistic effects among groups to optimize the hybrid NIPU system.

Therefore, the research and development of hybrid NIPU provides a new direction to meet the diverse needs of materials and shows great development potential. This section will focus on NIPU-epoxy resin hybrids, unsaturated compound hybrid NIPU, and siloxane-based hybrids, providing a detailed discussion of their types and synthesis methods.

3.2.1 Epoxy hybrid NIPUs. Cyclic carbonates have low reaction activation energy and can react under mild conditions. However, their limitations, such as slow reaction rate and insufficient rigidity, have prompted efforts to incorporate epoxy compounds to address these issues.⁶⁷ The synthesis of epoxy hybrid NIPU follows four main routes (A, B₁, B₂, and C) as shown in Fig. 4. Each route will be introduced in the following sub-sections.



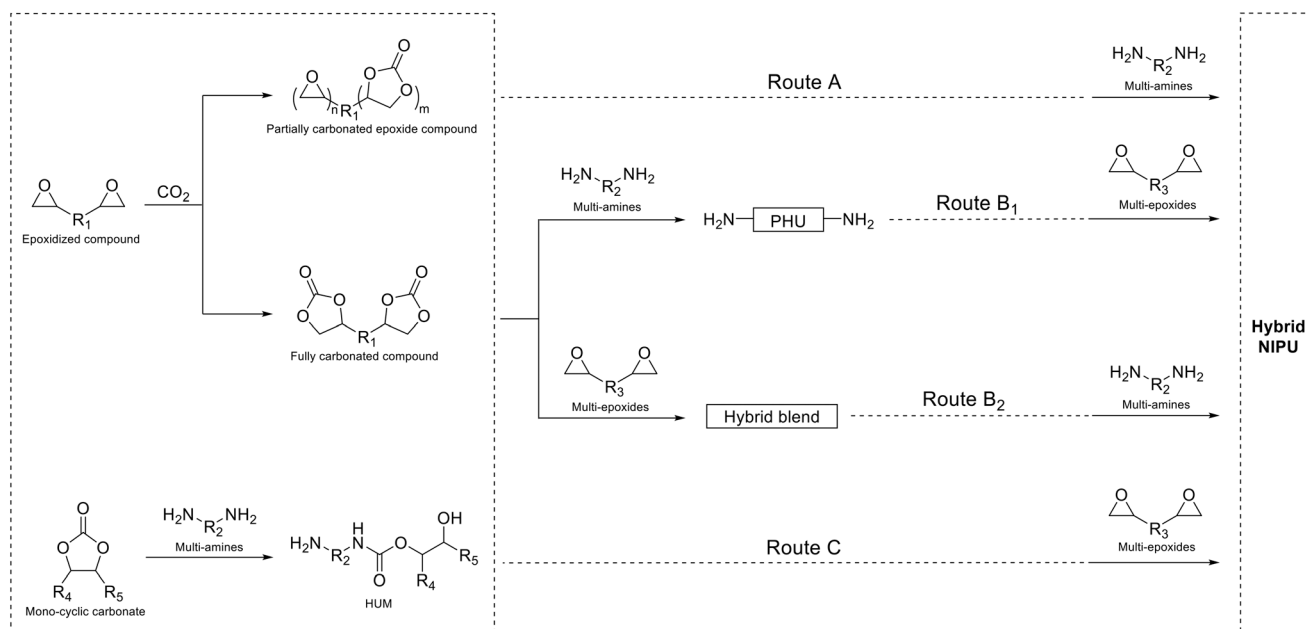


Fig. 4 Methods to synthesize NIPU-epoxy hybrid systems: (route A) partially end-carbonated hybrid systems; (route B) fully end-functionalized hybrid systems, including (route B₁) amino-telechelic systems and (route B₂) cyclic carbonate-telechelic systems; (route C) hydroxy-urethane modifier hybrid systems.¹⁹

3.2.1.1 Partially end-carbonated hybrid systems. Route A involves a two-step process: an epoxidized compound is first partially carbonated with carbon dioxide to form a compound containing both epoxide and cyclic carbonate groups. This partially carbonated epoxide compound is then reacted with multi-amines to produce a hybrid NIPU network.

The coexistence of epoxide and cyclic carbonate groups allows for two distinct ring-opening reactions with amines. Epoxides react rapidly and help increase crosslinking density and rigidity. In contrast, cyclic carbonates react more mildly and produce β -hydroxyurethane segments, which improve flexibility and reduce internal curing stress. The complementary reactivity and hydrogen bonding between polar groups improve the mechanical balance and facilitate network control. This synergistic behavior between epoxide and carbonate groups significantly accelerates the crosslinking process when they are used together.⁶⁸

By adjusting the ratio of epoxide to carbonate groups, researchers can fine-tune the crosslinking density and thermomechanical properties of the final polymer. Early studies by Rokicki *et al.* demonstrated that increasing cyclic carbonate content led to reduced peak exotherms, lower internal stress, and improved mechanical performance such as impact resistance, shear strength, and elongation.⁶⁹ Moreover, adjusting this ratio also helps reduce viscosity and shortens gel time during curing, thereby improving processability and enabling milder curing conditions.⁷⁰ These findings support route A as a robust and flexible design strategy for constructing hybrid NIPUs.

3.2.1.2 Fully end-functionalized hybrid systems. The fully end-functionalized hybrid routes can be categorized into amino-telechelic (route B₁) and carbonate-telechelic (route

B₂) systems, which differ significantly in crosslinking mechanisms and molecular interactions. The following sections will introduce their respective synthesis strategies and structure-property relationships.

As shown in route B₁ (Fig. 4), the amino-telechelic NIPU prepolymer is synthesized by reacting a fully carbonated compound with multi-amines, forming a PHU with terminal amino groups. This prepolymer then cross-links with epoxy resin, resulting in a three-dimensional hybrid network. The core of the method lies in the excess use of multi-amines and the precise control of the amine to epoxy ratio. During prepolymer synthesis, an excess of multi-amine is required to ensure complete conversion of cyclic carbonate groups and to obtain well-defined amino-terminated chains. If the amine content is insufficient, unreacted carbonate groups may remain, resulting in incomplete prepolymer structures. This compromises the subsequent epoxy curing step, reducing network integrity and overall material performance. Conversely, when the amine content is too high, the system tends to form more linear structures, lowering hardness and modulus while increasing elongation at break.⁷¹ In addition, replacing multi-amines with polyamines containing secondary amine groups can further accelerate their reaction with multi-epoxides, leading to an increased crosslinking density and a shorter gel time.⁷²

Mannari, *et al.* further developed a room-temperature curing coating based on amino-telechelic NIPU and successfully obtained a coating material that meets aviation industry standards by adjusting the amine/cyclic carbonate ratio and solvent composition. These coatings exhibited excellent chemical resistance and low-temperature flexibility ($-54\text{ }^{\circ}\text{C}$).⁷³ Zhang, *et al.* synthesized a two-component (2K



waterborne non-isocyanate polyurethane–epoxy hybrid coating using an amino-telechelic approach.⁵¹ Ling further developed this into a one-component (1K) waterborne NIPU coating system. This synthesis method enabled precise design of the soft and hard segment distribution, allowing flexible adjustment of the coating's flexibility and hardness by varying the ratio of prepolymers and hardeners. Consequently, the resulting coating exhibited significantly enhanced thermal stability, mechanical properties, and environmental resistance, providing an efficient solution for industrial coating applications.⁷⁴ These representative studies highlight how amino-telechelic hybrid NIPU systems can be tailored through molecular design and formulation optimization to meet demanding performance criteria. In particular, their compatibility with ambient-curing conditions and excellent mechanical-thermal balance make them strong candidates for high-performance coatings.

Route B₂ represents the cyclic carbonate-telechelic strategy. In this approach, cyclic carbonates are blended with multi-epoxides, and the mixture is then crosslinked using multi-amines to form a hybrid NIPU network. Compared with the chemical cross-linking of the amino-telechelic system, this system emphasizes the physical cross-linking of carbonate groups through intermolecular hydrogen bonds, which has unique advantages in improving mechanical properties and adjusting viscosity. Rokicki, *et al.* studied the effect of triethylene glycol diglycidyl ether bis-cyclic carbonate (TGDEC) on Epidian epoxy resin. They found that TGDEC significantly reduced the viscosity of the resin. As the TGDEC content increased, the gel time shortened, and the peak heat release decreased. At the same time, both impact strength and elongation at break improved.⁶⁸ Although the crosslinking density of the system was low (due to the lower activity of the functional group in cyclic carbonates than that in epoxy), it was found that the physical crosslinking of hydrogen bonds effectively compensated for this deficiency, allowing the material to achieve simultaneous growth in tensile strength and flexibility. In addition, the use of different cyclic carbonates has further demonstrated its potential in tuning material properties. Increasing the content of cyclic carbonates can improve the tensile strength and elongation at break. However, excessive content will reduce the crosslinking density, leading to lower mechanical strength and reduced thermal stability.⁷⁵ In general, the cyclic carbonate-telechelic NIPU system improves mechanical properties and processability by adjusting the ratio of carbonate, epoxy, and amine. Additionally, it helps to understand how hydrogen bonding influences material performance, providing a theoretical basis for further improvements.

3.2.1.3 Hydroxyurethane modifiers (HUMs) hybrid systems. In addition to the modification of the main chain, HUMs provide a unique synthesis path for the hybridization of epoxy in NIPU, which is complementary to the abovementioned methods (route C). HUM is synthesized *via* the reaction of a mono-cyclic carbonate with multi-amines, introducing the

hydroxyurethane group in the central region of the molecular chain. These groups are distributed in a comb-like structure along the polymer chain rather than concentrated at the end, which can accelerate epoxy-amine reactions. Blending HUM with multi-epoxides results in a hydroxyurethane-containing network, which provides a balanced combination of flexibility and rigidity.⁷⁶ Wazarkar, *et al.* further validated the potential of HUM in anti-corrosion coatings that combined the hardness provided by epoxy and the flexibility provided by hydroxyl carbamate units, while the suspended hydroxyl groups enhanced the adhesion to the substrate.⁷⁷ Unlike conventional epoxy–NIPU systems, where functional groups are mostly terminal, the integration of HUM introduces internal reactive sites and polar segments, improving toughness, interfacial adhesion, and network tunability. This HUM-based strategy, therefore, broadens the scope of epoxy–NIPU design, enabling advanced property control for functional coating applications.

3.2.2 Unsaturated compound hybrid NIPU. Exposure to environmental factors such as UV radiation, moisture, and temperature variations can affect the durability of NIPU, potentially limiting its application scope.⁷⁸ The introduction of unsaturated compound hybrid NIPU systems offers an effective strategy to enhance environmental resistance and broaden their practical utility. By incorporating unsaturated monomers such as acrylates, vinyl compounds, and styrene, these systems combine the flexibility of NIPU with improved weatherability, chemical resistance, and photopolymerization capability. As a result, they have been widely applied in adhesives, elastomers, and high-performance coatings.⁷⁹ As illustrated in Fig. 5, the synthesis strategies of such hybrid systems can be categorized into five distinct routes: A, B, C₁, C₂, and D. Detailed descriptions of each route will be provided in the following sub-sections.

3.2.2.1 Post-functionalization of unsaturated cyclic carbonate copolymers with amines. In this route (route A in Fig. 5), unsaturated cyclic carbonate monomers are first copolymerized with vinyl, acrylate, or styrene derivatives to form copolymers containing pendant carbonate groups. These side groups then undergo ring-opening aminolysis with amines to introduce β-hydroxyurethane segments and build the hybrid network. This two-step approach decouples the introduction of unsaturation from network formation, providing greater flexibility in controlling material structure and performance.

Boutevin *et al.* reviewed a wide range of unsaturated cyclic carbonates, including vinyl, allyl, styrenic, and (meth)acrylate types and summarized the polymerization behavior and aminolysis reactivity of these monomers.⁸⁰ Most studies focused on synthesizing copolymers with aliphatic backbones. These copolymers carry pendant carbonate groups that act as reactive sites for the post-functionalization with NIPU segments. For example, Kalinina *et al.* copolymerized 3-(2-vinyloxyethoxy)1,2-propylene carbonate (VOPC) with *N*-phenylmaleimide and post-functionalized the resulting copolymer using ethylenediamine (EDA) and hexamethylenediamine (HMDA). The resulting hybrid NIPU materials showed good solvent resistance and low moisture absorption, though limited adhesion and impact





Fig. 5 Synthetic routes for NIPU-unsaturated compound hybrid systems: (route A) post-functionalization of unsaturated cyclic carbonate copolymers with amines; (route B) synthesis of hydroxyurethane methacrylates (HUMAs); (route C) introduction of double bonds into NIPU via hydroxyl group functionalization, including (route C₁) incorporation of unsaturated double bonds into side chains of the NIPU backbone and (route C₂) incorporation of unsaturated double bonds into terminal groups of the NIPU backbone; (route D) direct reaction of amines with compounds containing double bonds.⁶⁶

strength.⁸¹ In another study, Webster and Crain synthesized copolymers based on vinyl ethylene carbonate (VEC) and reacted them with various primary amines. The solvent resistance was improved by increasing amine content, reaching a maximum at the stoichiometric ratio 1.0–1.2. The resulting coatings exhibited good gloss, pendulum hardness, and mechanical durability.⁸²

An alternative approach shares the same goal. It involves the simultaneous ring-opening of cyclic carbonates and radical crosslinking of unsaturated groups. Although more direct, this method offers less control over the resulting network structure. It has also been associated with gelation or reduced mechanical performance in some systems. Therefore, this approach is not illustrated in Fig. 5.

3.2.2.2 Hydroxyurethane methacrylates (HUMAs). As shown in route B (Fig. 5), hydroxyurethane modifiers (HUMs) are first synthesized *via* the ring-opening reaction between mono-cyclic carbonates and amines, introducing hydroxyl-terminated urethane groups. These HUMs are then further functionalized with methacrylate monomers, typically methacrylic anhydride or methacryloyl chloride, to yield (hydroxy)urethane methacrylates (HUMAs). Finally, the resulting HUMAs undergo radical polymerization to form the NIPU-acrylic hybrid networks.

HUMAs exhibit low viscosity and multifunctionality, enabling rapid formation of compact networks under UV irradiation. These features make them ideal candidates for UV-curable adhesives and 3D printing applications, especially

where fast curing and low energy consumption are critical.⁸³ Beyond their curing speed, HUMAs offer excellent structural tunability. Owing to their short-chain architecture and well-defined functional groups, their molecular structure is highly controllable. By adjusting the degree of methacrylation or preserving hydroxyl functionalities, the crosslink density, polarity, and hydrogen bonding interactions can be precisely tuned. This multi-level design flexibility enables a broad spectrum of mechanical properties, ranging from soft and extensible to rigid and durable systems.⁶⁶ Additionally, HUMAs possess moderate molecular weight and a balanced hydrophilic/hydrophobic profile, which ensure good compatibility with a variety of resins, such as acrylics, epoxies, and polyesters. This advantage contrasts with highly viscous or overly crosslinked resins, which often suffer from poor miscibility and processing limitations.⁸³

3.2.2.3 Introduction of double bonds via functionalization of hydroxyl groups on NIPU chain ends or side chains. In NIPU systems, polymerizable double bonds can be introduced *via* two common strategies: functionalization of side-chain hydroxyl groups (route C₁) or modification of terminal hydroxyl groups (route C₂). Although both approaches produce UV-curable or thermally curable prepolymers, the position of the double bonds leads to distinct differences in crosslinking behavior and tunability of material properties.

Route C₁ typically involves the polyaddition of bis-cyclic carbonates and diamines to produce PHUs with pendant hydroxyl groups. These hydroxyls are then functionalized





Fig. 6 Synthetic strategies involving siloxane/silane groups: (route A) cyclic carbonate-functionalized siloxane/silane strategy; (route B) amino-functionalized siloxane/silane strategy.

with vinyl-containing monomers, introducing multiple polymerizable groups along the backbone and enabling high functionality and uniformly crosslinked networks. Ochiai *et al.* synthesized methacrylate-functionalized PHUs using this method, which exhibited good mechanical strength, solvent resistance, and tunable crosslinking behavior—making them suitable for high-performance thermosetting materials.⁸⁴ In contrast, route C₂ starts from mono-cyclic carbonates and diamines to form hydroxyl-terminated oligomers. These oligomers are subsequently reacted with methacrylate-type monomers to introduce terminal double bonds. Han *et al.* employed this route to prepare UV-curable unsaturated poly(ester-urethane)s, whose cured coatings exhibited good flexibility and adhesion. Their overall performance was comparable to that of commercial polyurethane acrylate coatings.⁸⁵

Therefore, route C₁ is more suitable for rigid, highly crosslinked UV-curable systems, while route C₂ is better suited for flexible network materials. The selection of route should depend on the performance requirements of the target application.

3.2.2.4 Direct reaction of amines with double bonds (aza-Michael addition reaction). Aza-Michael addition is also a useful strategy for introducing double bonds into NIPU networks. This reaction occurs between amine groups and electron-deficient unsaturated compounds and is referred to as route D (Fig. 5). As illustrated in the scheme, bis-cyclic carbonates are first reacted with diamines to synthesize PHUs. By using a slight excess of diamine during the reaction, residual primary amine groups remain at the chain ends of the resulting PHU oligomers. These amines can subsequently react with the vinyl groups of acrylate-type compounds to introduce unsaturated moieties into the NIPU structure.

A key advantage of this method lies in its mild and environmentally friendly reaction conditions. According to Bassam *et al.*, the aza-Michael addition proceeds efficiently at

temperatures between 50–80 °C, without requiring any catalyst, and can be carried out solvent-free or in green solvents such as dimethyl carbonate.⁸⁶ This approach not only simplifies the functionalization process but also facilitates the design of crosslinkable NIPU materials under sustainable and scalable conditions.

3.2.3 Siloxane/silane hybrid NIPU. The introduction of siloxane/silane groups gives hybridized NIPU materials unique properties, such as high flexibility, hydrophobicity, and thermal stability.^{46,87} According to the different synthesis routes (Fig. 6), silicon-based NIPUs can be synthesized through a sol-gel process from cyclic carbonate-functionalized siloxane/silane groups (route A) or through amino-functionalized siloxane/silane groups (route B). The chemical characteristics and molecular structure of the siloxane/silane groups influence the final performance of the hybrid NIPU.

The cyclic carbonate-functionalized siloxane/silane strategy works by binding cyclic carbonate groups to siloxane/silane molecules, which then react with diamines to form NIPU networks. Incorporation of siloxane/silane segment improves flexibility primarily due to their flexible Si–O–Si bonds and low internal rotational barriers. Additionally, their low surface energy increases polymer chain mobility, resulting in enhanced flexibility and hydrophobicity of the resulting materials. Liu, *et al.* studied polysiloxanes with cyclic carbonate side chains that were reacted with diamines to produce silica-based PHU materials.⁸⁸ Their results confirmed the enhanced flexibility and hydrophobicity of the resulting coatings. Caillol, *et al.* obtained a low-viscosity silicone-based PHU material by carbonating the epoxy group in the siloxane skeleton using CO₂ to form cyclic carbonate, which was further reacted with diamine.⁸⁹ This material exhibits high crosslinking density and excellent thermo-mechanical properties.

Siloxane/silane groups can be effectively introduced into the NIPU network through the reaction between amino-functionalized siloxane compounds and cyclic carbonates. Figovsky and Shapovalov developed epoxy-PHU hybrid NIPU





Fig. 7 Synthesis pathway of vegetable oil-based cyclic carbonate.

coatings using amino-functionalized siloxane compounds. Under ambient humidity, siloxane groups undergo hydrolysis, forming silanol ($-\text{SiOH}$) groups. These silanol groups subsequently undergo condensation and crosslinking within the NIPU network. This crosslinking reaction enhanced the material's adhesion by promoting stronger interfacial interactions and improved corrosion resistance by creating a more compact, hydrophobic network structure that inhibited penetration of corrosive substances.⁹⁰ Narayan, *et al.* designed a siloxane compound with an amine group that reacts with cyclic carbonates to form a high-branched or linear silicon-based polymer.^{91,92} Under the condition of no water, the reaction generated a high-branch network. Under acidic conditions, a linear structure was formed, showing the significant influence of different reaction conditions on the material structure. Gomez-Lopez, *et al.* designed a high-performance adhesive using a siloxane compound with an amine group, which formed a cross-linking network by reacting with bicyclic carbonate, greatly improving the bonding strength and thermal stability.⁹³

The siloxane/silane hybrid NIPU system shows similar functional characteristics regardless of the introduction method, with its superior performance primarily attributed to the tailored structure of the siloxane and hybrid groups. The introduction of siloxane gives the material excellent thermal stability and weather resistance, significantly improving the material's resistance to polar solvents and harsh environments. In addition, these hybrid materials exhibit excellent adhesion, and the unique chemical properties of siloxanes provide superior flexibility and elasticity. Low-viscosity silicon-based materials also have high processing efficiency and meet the needs of industrialization, especially in the fields of coating, sealants, and adhesives. Moreover, introducing siloxane groups through the reaction of cyclic carbonates with amines is a straightforward and versatile method. By selecting suitable amino-functionalized siloxane compounds, material properties can be precisely tuned, effectively balancing overall performance with ease of processing. In short, siloxane hybrid NIPUs offer an outstanding balance between performance and processability, making them particularly suitable for applications requiring comprehensive material properties, such as advanced coatings, industrial sealants, and adhesives. It is worth noting that similar molecular design strategies can also be applied to introduce other functional groups into the NIPU network. These groups can be incorporated simply and efficiently through the aforementioned methods, enabling precise tuning of material properties to meet specific performance requirements.

4. Bio-based precursors for NIPU

4.1 Vegetable oils

Vegetable oils are a promising bio-based feedstock due to their biodegradability, low cost, non-toxicity, eco-friendliness, and low greenhouse gas emissions during production. Derived from plant products such as seeds and grains, vegetable oils contain unsaturated and ester functionalities that facilitate modification. A common modification approach is epoxidation, followed by carbonation with CO_2 to produce cyclic carbonate, as shown in Fig. 7.⁹⁴ The resulting cyclic carbonate can then react with amines to form NIPU.

Various vegetable oils, including soybean oil, linseed oil, and sunflower oil, have been studied and applied in NIPU synthesis.^{95–97} Tamami, *et al.* first developed NIPU from vegetable oil. Epoxied soybean oil was reacted with CO_2 , catalyzed by tetrabutylammonium bromide at 110 °C for 70 h, yielding 94%. The study investigated the effects of stoichiometric balance and amine type on the final NIPU properties. Results indicated that as stoichiometric balance was achieved, the extractable content decreased, while T_g and stress increased. Also, triamine showed the lowest soluble fraction, strain at break, and the highest T_g and stress.⁹⁸ Farhadian, *et al.* synthesized 100% bio-based NIPU from vegetable oils. Sunflower oil was epoxied at 50 °C for 7 h, then carbonated by CO_2 at 100 °C for 30 h. In addition, different amines were synthesized from castor oil, oleic acid, or epoxide sunflower oil. Final NIPU synthesis was achieved at 90 °C for 24 h. Due to the amide, ester, and hydroxyl groups in the amine structure and its high molecular weight, the resulting NIPU demonstrated enhanced thermal stability, with decomposition temperature reaching up to 386 °C.⁹⁹ However, modified vegetable oils typically exhibit low reactivity because of the internal cyclic carbonate groups, necessitating a reaction temperature above 100 °C to obtain NIPU. Mokhtari, *et al.* improved this by modifying jojoba and castor oils with pendant cyclic carbonate groups through thiol-ene coupling with thioglycolic acid, followed by esterification with glycerin carbonate. As shown in Fig. 8, the novel cyclic carbonates exhibited higher reactivity, allowing the NIPU synthesis at 40 °C and without the need for a catalyst.¹⁰⁰

Similarly, Ling, *et al.* also functionalized the linseed oil to create waterborne NIPU coatings. These coatings were synthesized from linseed oil-based cyclic carbonate, bio-based fatty acid diamine, and 3,3'-diamino-*N*-methylpropylamine (DMDPA). The study revealed that formulations with higher



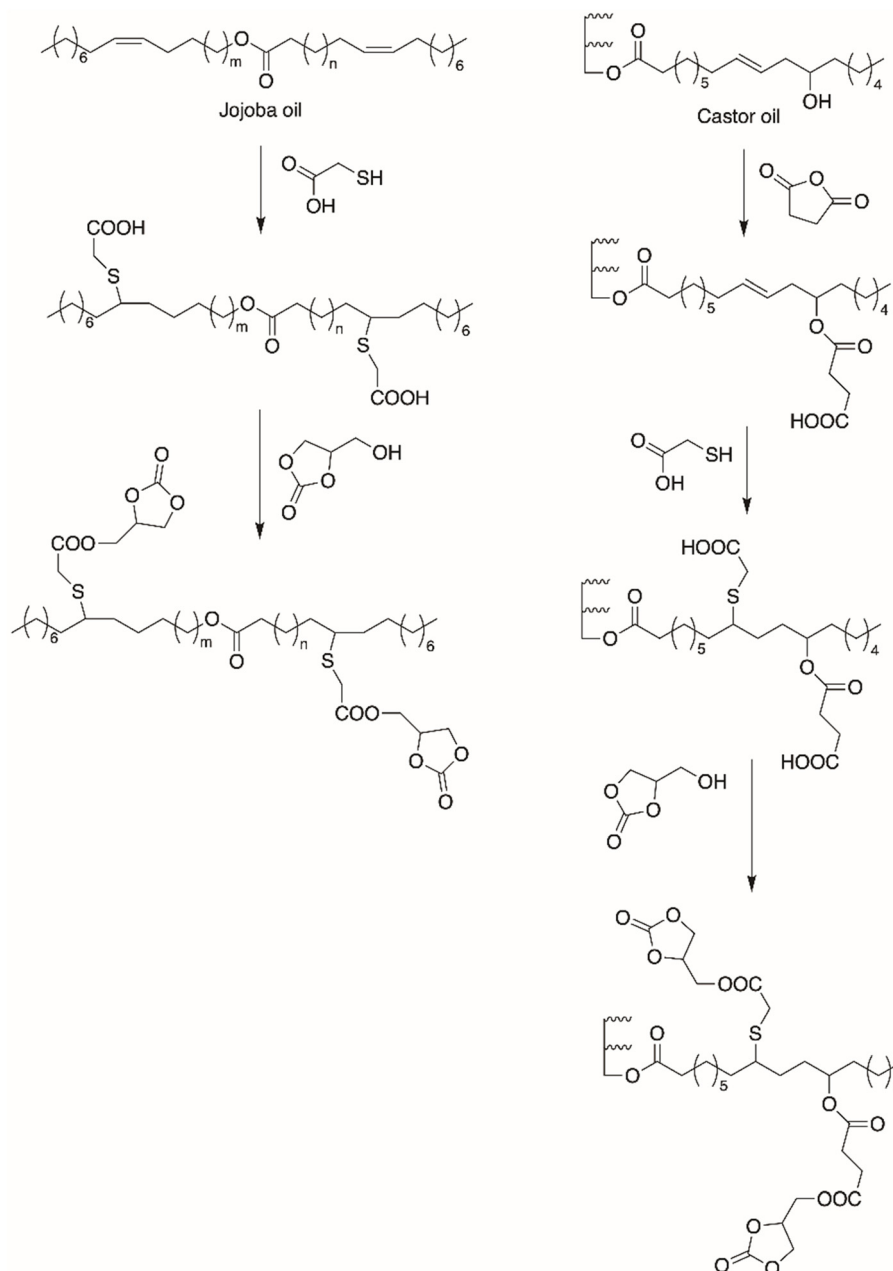


Fig. 8 The modification of jojoba and castor oils.¹⁰⁰

DMDPA content exhibited increased T_g and mechanical strength, though with reduced elongation and thermal stability.⁵²

4.2 Lignin

Lignin is a complex aromatic polymer found in most terrestrial plants, offering potential as a renewable replacement for petroleum feedstocks in aromatic NIPU due to its rich aromatic structure.¹⁰¹ However, bulk lignin shows limited reactivity because reactive sites are often hindered by plant cell walls.^{102–104} The general pathway for converting lignin to NIPU, as shown in Fig. 9(a), begins with the carbonation of lignin's hydroxyl groups

to form lignin-based cyclic carbonates, which then react with amines to yield NIPU. Two primary methods are used to synthesize lignin-based cyclic carbonate: transesterification and epoxidation, followed by carbonation. Fig. 9(b) illustrates the transesterification approach, where oxyalkylate lignin is synthesized by reacting Kraft lignin with glycerol carbonate, followed by cyclocarbonation with dimethyl carbonate.¹⁰⁵ Oxyalkylation may lead to other bonds, like ether linkages.^{106,107} Fig. 9(c) shows the lignin modification through epoxidation and CO₂ fixation. In this process, lignin hydrogenolysis oil (LHO) is first reacted with epichlorohydrin to produce an LHO chlorohydrin intermediate. Subsequent NaOH catalysis facilitates the formation of an epoxy ring, which is then reacted with CO₂





Fig. 9 (a) Synthesis route of lignin-based NIPU. (b) Lignin-based cyclic carbonate by transesterification.¹⁰⁵ (c) Lignin-based cyclic carbonate by epoxidation and carbonation.¹⁰⁸

under the catalysis of quaternary ammonium salt to yield LHO cyclic carbonate.¹⁰⁸ Besides carbonation, lignin can also be modified to produce amines for NIPU synthesis. Typically, lignin oligomers or lignin-derived monomers, like vanillin, are used due to their aldehyde groups, which make them suitable precursors for lignin-based amines. For instance, Fache and co-workers obtained vanillin-based diamines through reduction, decarboxylation, or oxidation in the first step, then underwent allylation followed by a thiol-ene reaction with cysteamine hydrochloride.¹⁰⁹

4.3 Cardanol

Cardanol, the primary component of cashew nutshell liquid (CNSL), features a long aliphatic chain, a rigid aromatic ring, and phenolic hydroxyl groups, making it a promising starting material for NIPU preparation.¹¹⁰ Kathalewar, *et al.* prepared NIPU coating from CNSL-based cyclic carbonate and amines. The cyclic carbonate was obtained by fixing CO₂ onto CNSL-based epoxy for 10 h under TBAB catalyst at 120 °C and 1000 psi (Fig. 10).¹¹¹ Instead of cyclic carbonate, amines can also be prepared from cardanol; Laprise, *et al.* developed NIPU using fish oil-based cyclic carbonate in combination with Cardolite NC-540, a commercial phenalkamine mixture derived from CNSL.¹¹²

4.4 Other bio-based feedstocks

Besides vegetable oil, lignin, and cardanol, several other bio-based feedstocks are being explored for NIPU synthesis. Bähr,

et al. developed NIPU from limonene dicarbonate, a member of the terpene family. Terpenes are highly unsaturated and ester-free bio-based resources. In this study, limonene dioxide was reacted with CO₂ to produce the corresponding dicarbonate.¹¹⁴ Additionally, Choong, *et al.* synthesized NIPU with high bio-content from hydroxymethylfuran bis(cyclic carbonate) and 2,5-bis(aminomethyl)furan. Both of these bio-based materials can be derived from carbohydrates. The furan-containing bio-based NIPU exhibited self-healing properties at room temperature and under dry conditions.¹¹⁵

5. Potential applications of bio-based NIPU

Polyurethanes have good adhesion, flexibility, high cohesive strength, and performance at low temperatures, which makes them have manifold applications in adhesive, sealant, paint, and coating. Biobased NIPU has been studied for use as greener alternatives in these fields. This section focuses on studies applying biobased NIPU at interfaces like coatings and adhesives.

5.1 Coatings

In recent years, there has been a growing interest in developing NIPU coatings as a more sustainable alternative to their isocyanate-based counterparts. NIPU coatings were reported to have excellent adhesion properties on the metal





Fig. 10 Synthesis of cardanol-based cyclic carbonate.¹¹³

substrate and chemical resistance. Recently, Sulthana, *et al.* synthesized castor oil-based NIPU and NIPU nanocomposite (NIPU-F) coatings. The NIPU-F was achieved by incorporation of amine-modified silica-coated Fe_3O_4 nanoparticles into the NIPU *via* a covalent bond. The NIPU coatings showed antibacterial and anti-fouling properties. As shown in Fig. 11, NIPU and NIPU-F showed fewer algae on the surface than the blank group.¹¹⁶

Moreover, Saha, *et al.* prepared the NIPU from oleic acid-based cyclic carbonate through microbial conversion. The NIPU showed less than 20% of water absorption and less than 5% of UV transmittance, proving its potential application in protective coating and food packaging.¹¹⁷ Furthermore, Silbert, *et al.* reported bio-based NIPU coatings from soybean oil-based polycarbamate, biobased dialdehyde, and petroleum-based dialdehyde. The coating exhibited 67–150 °C T_g , 70–143 König hardness, and 2B-H pencil hardness; however, the coatings were showing brittleness, hence limiting the impact resistance.¹¹⁸ Pouladi, *et al.* synthesized NIPU coatings by curing linseed oil-based cyclic carbonate with diethylenetriamine. By controlling the conversion percentage of linseed oil carbonation, the coatings achieved

different mechanical, physical, and anti-corrosion properties. Among that, the sample using 75% carbonation cyclic carbonate showed the lowest impedance reduction after a 336 h immersion test in 3.5 wt.% NaCl solution characterized by electrochemical impedance spectroscopy, indicating better corrosion resistance.¹¹⁹

Choong, *et al.* prepared the succinic acid-based NIPU coatings, where succinic acid can be produced from bio-based feedstock. The NIPU coatings exhibited good resistance to water and toluene, but poor resistance to acid and alkali. The coating was dip-coated onto the curved metallic surface and showed good corrosion resistance, as shown in Fig. 12.¹²⁰

5.2 Adhesives

PU has become widely used in the adhesive field since its inception. They are applied on extensive surfaces, including glass, wood, plastics, ceramics, *etc.* In recent years, researchers have turned their focus towards the development of bio-based NIPU adhesives because of the growing recognition of the environmental and fossil fuel shortage concerns.⁶⁴



Fig. 11 (a) Fluorescence microscopy images and (b) number of algal cells in the blank group and NIPU coatings. Reproduced with permission from ref. 116. Copyright 2024 RSC.





Fig. 12 Digital photos of uncoated copper substance: (a) experimental setup, (b) before, and (c) after corrosion test. Photos of coated substance: (d) before and (e) after corrosion test. Reproduced with permission from ref. 120. Copyright 2024 Elsevier.

Patel *et al.* synthesized bio-based NIPU adhesives from carbonated soybean oil and different amines through a solvent and catalyst-free approach. The adhesives were applied on oak wood, and the tensile strength was between 6.23–8.26 MPa.¹²¹ In another work, Zhang, *et al.* produced the bio-based NIPU adhesive from cashew phenol.¹³ The adhesive can bond different substances and maintain good adhesion under low temperatures, and the steel substance can support a 60 kg weight at $-37\text{ }^{\circ}\text{C}$, as shown in Fig. 13.

Zhou, *et al.* synthesized rosin-based NIPU and explored its self-healing and recycling properties for adhesives. Rosin is a bio-based feedstock and can be easily acquired. In this study, rosin reacted with fumaric acid through Diels–Alder cycloaddition to obtain the fumaropimaric acid, which was further modified to fumaropimaric acid cyclic carbonate and then crosslinked with polyethyleneimine. The adhesive has

good lap shear strength when applied to wood boards. As shown in Fig. 14, the adhesive also exhibited self-healing behavior after a scratch.¹²²

5.3 Biomedical applications

Currently, PU for biomedical applications only occupies a small part of the whole production of PU, and NIPU is even less so. The regulation for biomedical applications has strict requirements about cytotoxicity, acute and subchronic toxicity, as well as hemocompatibility and carcinogenicity.¹²³ Bio-based NIPUs for biomedical applications have achieved great progress in the last few years. Aduba Jr., *et al.* electrospun the plant oil-based NIPU mats. It was found that the poly(tetramethylene oxide)-containing NIPU mats have no cytotoxicity.¹²⁴ Laurén, *et al.* reported the 3D printable

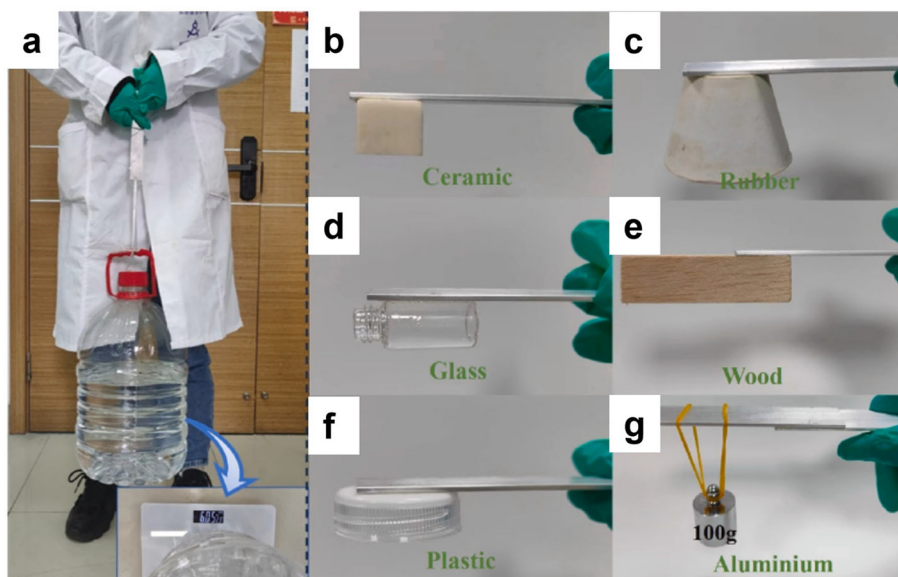


Fig. 13 Digital images of (a) weight support of the steel substance adhered by the NIPU adhesive exposed under $-37\text{ }^{\circ}\text{C}$. (b)–(g) adhesion of NIPU to different substances. Reproduced with permission from ref. 13. Open access: *Polym. Test*.





Fig. 14 Self-healing behavior of the NIPU adhesive after a scratch. Reproduced with permission from ref. 122. Copyright 2024 Elsevier.



Fig. 15 (a) photo of NIPU hydrogel, (b)–(d) cross-section and surface SEM images of the hydrogel matrix. Reproduced with permission from ref. 125. Open access: *Int. J. Biol. Macromol.*

hydrogels, which contain antibacterial double-quaternized chitosan (DQC), NIPU, and TEMPO-oxidized cellulose nanofibrils (CNF) that were used to modify the 3D printability and hydration behavior of the hydrogel. The 3D

matrix was printed by direct ink writing technology and crosslinked by the intermolecular hydrogen bonding. The hydrogel showed a porous structure and uniform morphology (Fig. 15). In addition, the cell proliferation was enhanced

Table 2 Commercialization snapshot of NIPU technologies

Application field	Representative product/example	Commercialization stage ^a	Key advantages claimed	Ref.
Coatings	TRUE Green Poly™	Full commercial launch	Zero-isocyanate, VOC ≈ 0, durability comparable to PU/epoxy, 30–60% lower application cost	126
	Green Polyurethane™ coating	Full commercial launch	Zero-isocyanate, superior durability vs. competitor acrylic-PU topcoats	127
Adhesives/sealants	Collano hybrid NIPU structural adhesive	Pilot-scale & limited commercial supply	Room-temperature cure, strong bonding to wood & metals, fully isocyanate-free	128
	Green Polyurethane™ adhesive line	Early commercial/JV development	Zero-isocyanate 2K adhesive, targeted at industrial sealant/adhesive markets	129
Medical/biomedical	3D-printable NIPU elastomers for implants	Research stage TRL 4	Photo-curable PHU elastomer, hemocompatible, customizable lattice structures	130
	Double-quaternized chitosan–NIPU–CNF hydrogel dressing	Research stage TRL 4	Injectable/printable, porous & shape-stable, biocompatible, initial antibacterial activity	131

^a Commercialization stage codes: full commercial launch = regular market sales with public product datasheet. Pilot/limited commercial = specific or B-to-B supply, announced but not yet widely distributed. Research stage = pre-commercial, lab, or early prototype only. TRL = technology readiness level.



with the incorporation of DQC, making it possible for wound healing.¹²⁵

5.4 Commercial readiness

Moving NIPU technologies from laboratory breakthroughs to marketable products is a central goal of current research. To make the industrial maturity of NIPU technologies more transparent, a commercialization snapshot that covers coatings, adhesives, and biomedical uses is summarized in Table 2. Commercial readiness is grouped into three levels: full commercial launch, pilot or limited commercial supply, and research stage.

Table 2 shows a clear gradient across application fields. Coating products such as TRUE Green Poly™ have reached regular market sales, demonstrating the technical and economic viability of NIPU chemistry.^{126,127} Adhesive systems are in pilot production but still face cost and cure-speed constraints.^{128,129} Biomedical implementations remain at the research stage because they must satisfy ISO 10993 biocompatibility and GMP raw-material requirements.^{130,131} Taken together, these observations show that the NIPU platform as a whole is still in its commercial infancy. Moving beyond specific coatings will require faster-curing formulations, scalable and cost-effective cyclic-carbonate supply chains, standardized test methods, and larger-scale demonstration projects.

6. Conclusions

This review summarizes the synthesis procedures and types of NIPU, common raw materials for bio-based NIPU, and the potential applications of bio-based NIPU. Research on bio-based NIPU has progressed greatly in the past years, and more synthesis strategies have been developed. Due to the versatile choices of bio-feedstocks and multiple modification methods of the materials, bio-based NIPU has shown great potential in different application fields, especially at the interface, such as coating, adhesive, and wound curing. However, there are many challenges for the real application and industrial production of bio-based NIPU. First, the synthesis for bio-based NIPU usually requires many steps, as well as different post-processing, decreasing the yield and increasing the energy consumption of the materials. The slow polymerization of NIPU also hinders the scale-up production. In addition, the cost of bio-based raw materials is fluctuating in the market due to many factors and is not comparable to most petroleum-based raw materials; this is also a key factor in limiting industrial production. Most importantly, the conventional PU has better overall performance than that of bio-based NIPUs, even though some bio-based NIPUs already show comparable performance in some specific properties. These limitations are major factors that have prevented it from completely replacing PU so far. Therefore, the improvement of synthesis procedures, optimization of reaction conditions, and further understanding of structure–

property relationships are still needed in the future for scalable production and commercialization.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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