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Cutting-edge development of non-isocyanate polyurethane (NIPU) foams: from sustainable precursors to environmental impact evaluation

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Polyurethane (PU) foams represent a wide class of polymeric materials, having applications in different sectors ranging from automotive, packaging, and cushioning/bedding to construction. However, their synthesis requires the use of petrol-based components, which are mostly harmful and toxic isocyanates. Considering this, non-isocyanate polyurethane (NIPU) foams have been demonstrated to be promising alternatives to conventional PUs, which are obtained through “isocyanate-free” routes such as the aminolysis of cyclic carbonates with diamines. The building blocks of NIPU foams can be derived from different bio-sources, such as vegetable oils, sugars, and terpenes. Moreover, the final NIPU materials can be fully reprocessed and recycled owing to the presence of suitable functional groups that facilitate dynamic bond exchange. This review aims to comprehensively describe the current state-of-the-art concerning the synthesis and applications of NIPU and hybrid NIPU foams and is divided into three sections: (i) an outline of the synthesis of bio-based NIPU precursors, *i.e.* cyclic and linear carbonates, diamines and carbamates, from biomass-derived and waste sources such as vegetable oils and CO₂ and *via* environmentally friendly approaches; (ii) analysis of the reprocessability and recyclability of NIPU and composite NIPU foams; and (iii) evaluation of the environmental impacts of NIPU precursors and foams using the life cycle assessment (LCA) technique, preliminary investigations of their techno-economic analysis (TEA), and description of future perspectives.

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1. The main advances in green chemistry related to the synthesis of sustainable polyurethanes, namely, NIPU (non-isocyanate polyurethane), were discussed.
2. This review article focuses on a hot topic as the produced NIPU could be used for a wide range of applications. Moreover, this review is multidisciplinary, linking chemistry, reaction engineering, polymer syntheses and characterization.
3. Our work can inspire the further development of new synthetic routes to produce NIPU, leading to the development of chemical processes to produce sustainable polyurethanes.

1. Introduction

In the last decades, considerable attention has been paid to polyurethanes (PUs), making them the 6th most used polymers around the world¹ and one of the most versatile raw

materials for various chemical structures including, foams, elastomers, sealants, and coatings. Among these, PU foams are the largest subgroup, representing more than 60% of the overall PU market.² They are key materials for modern life, with a broad range of applications in bedding/cushioning (furniture, mattresses, and seats), thermal/acoustic insulation^{3–5} and shock and water adsorption.⁶ In 2022, the worldwide production of PU foams was USD 46.80 billion (about 8% of the overall plastic market), which is expected to reach USD 78.16 billion by 2029⁷ (10% of the worldwide plastic market) with a compound annual growth rate (CAGR) of 4.5%.

Generally, PUs are obtained *via* the polyaddition of polyols (containing reactive hydroxyl groups) and di-isocyanates

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(Scheme 1i) followed by a blowing process, which is triggered by physical or chemical blowing agents (BAs). Physical BAs, such as hydrofluorocarbons (HFCs), hydrocarbons (HCs) and hydrofluoroolefins (HFOs),^{8,9} are volatile compounds that evaporate to the gas phase owing to the exothermicity of the reaction. Alternatively, chemical BAs generate blowing gas through chemical reactions. For example, water and formic acid can act as chemical BAs, reacting with isocyanate and generating unstable carbamic acid.⁸ The latter decomposes into amine and CO₂, causing blowing^{10,11} (Scheme 1, ii).² As a side reaction, urea is formed from the reaction between the isocyanate and amines (Scheme 1, iii).¹²

Typically, PU precursors are obtained from petrol-based sources. The synthesis of PU foams involves the use of isocyanate products, *i.e.* methylene-diphenyl di-isocyanate (MDI) and toluene di-isocyanate (TDI), which are obtained using extremely toxic phosgene. Moreover, prolonged exposure to isocyanate products poses significant issues to human health such as dermatitis, eye irritation, and respiratory diseases (asthma).¹⁴ Many of them are indeed classified as CMR, *i.e.*, carcinogenic, mutagenic, and reprotoxic.¹³ In August 2020, the European Union promoted a REACH restriction (ANNEX XVII),¹⁵ which limits the use of di-isocyanates (cut-off limit is 0.1%) and introduced mandatory training for employees handling di-isocyanates.

The ongoing challenge in the scientific community is to shift to 100% bio-based raw materials, while maintaining an enhanced functional performance in the final foamed materials. In the past 20 years, both the research community and industry have devoted significant efforts to finding strategies to reduce CO₂ emissions and shift from petrol-derived materials to more sustainable sources and technologies. Among them, a common approach involves replacing petrol-

based polyols with bio-based polyols employing renewable building blocks derived from either microbial^{16–18} or lignin-cellulosic biomass^{19,20} as well as plant oils.^{21–23} However, although the use of bio-based polyols is a great step forward, the presence of isocyanates enormously affects the transition towards a total green process. Therefore, bio-based isocyanates derived from terpenes, fatty acids, lignin, and amino acids have been developed.^{24,25} Some of them have already appeared on the market, such as aliphatic isocyanates, *i.e.* Lupranat® ZERO by BASF,²⁶ Desmodur® QCN 3000 by Covestro,²⁷ and Tolonate X FLO 100 by Vencorex.²⁸ Nevertheless, the toxic phosgene is still partially employed in the manufacturing of the latter products.

The synthesis of non-isocyanate polyurethanes (NIPUs) has been strongly encouraged in the last decade,^{29–32} despite their initial discovery in 1957 by Dyer and Scott.³³ To date, many isocyanate-free alternative pathways have been reported in the literature. Among them, the aminolysis of linear (LCs) and cyclic carbonates (CCs) with diamines^{34–37} and transurethanization of bis-alkylcarbamates/bis-hydroxyalkylcarbamates with alcohols³⁸ are considered the most promising routes to obtain NIPU foams, as illustrated in Fig. 1.

The aminolysis of dicarbonates with diamines is a solvent-free route resulting in the formation of hydroxy-urethane repeating units and generating the so-called polyhydroxyurethanes (PHUs).^{34,35} Usually, acid/base catalysts are employed to enhance the reaction rate³⁵ but this process also proceeds under catalyst-free conditions.³⁹ CCs with 5-membered rings (5CCs) are preferably used as monomers for the synthesis of NIPU. They can be obtained through sustainable pathways such as cycloaddition of CO₂ to epoxidized vegetable/biomass-derived oils, *i.e.*, sunflower, linseed, and cardanol oils.^{35,40–42} Recently, terpenes, tannin or lignin derivatives, vanillin, and



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Her research explores the integration of bio-based functional fillers to enhance the properties of materials for various applications. Additionally, she investigates the reprocessability and recyclability of these materials to promote sustainable end-of-life solutions.

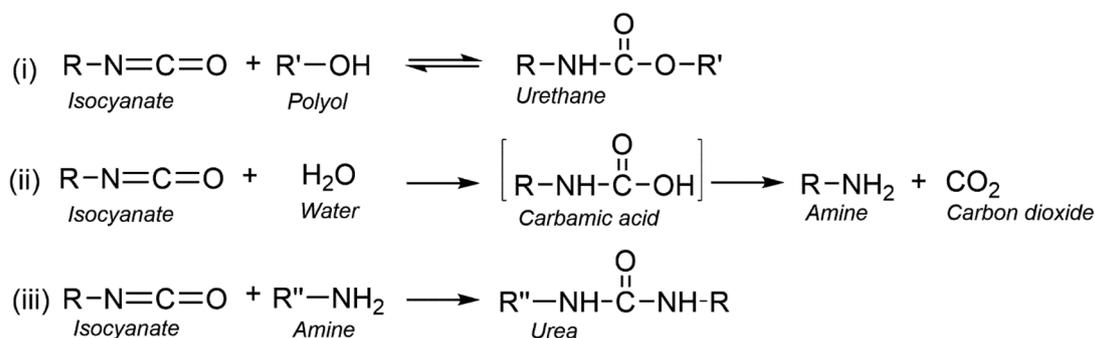


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polyurethane foams derived from renewable and natural resources. Her research explores the integration of bio-based functional fillers to enhance the properties of materials for various applications. Additionally, she investigates the reprocessability and recyclability of these materials to promote sustainable end-of-life solutions.





Scheme 1 Synthesis of conventional PU foams: (i) polyaddition between isocyanate and polyol, (ii) blowing reaction between isocyanate and water and (iii) reaction between isocyanate and amine, whereby polyurea is obtained.

glycerol⁴³ have been proposed as sustainable building blocks to obtain these precursors. Diamines are usually petrol-based sources; however, they may also be obtained using sustainable building blocks such as fatty acid dimerization.⁴⁴

The main drawback of the aminolysis pathway is the relatively low reactivity of CCs with diamines, which requires a very long reaction time, limiting the scalability of the process on an industrial level. Thus, to overcome this limitation, new approaches have been developed involving the use of thiols and thiol derivatives.⁴⁵ More specifically, employing thiols in the formulation of CCs and diamines accelerates the decarboxylation of CCs, also enhancing the aminolysis process. Either linear thiols or cyclic dithiocarbonates (CTCs) can be employed, which exhibit higher reactivity towards amines.^{45,46} Actually, it has been demonstrated that the reaction time can be reduced from several hours to minutes.⁴⁵ The backbone of the resulting polymers possesses both urethane and

thioether linkages. Therefore, they are defined as non-isocyanate polyhydroxythiourethanes (NIPTU) due to their hybrid nature.⁴⁵

Another attractive route to obtain NIPUs is the transurethanization (or polycondensation) of carbamates with alcohols. Nowadays, alkylcarbamates can be synthesized *via* phosgene-free routes, *e.g.*, reactions involving dialkylcarbonates and diamines, making transurethanization safer than the traditional route. In contrast to aminolysis, transurethanization leads to the formation of urethane moieties rather than to hydroxyurethane moieties. Therefore, the resulting chemical structure is closer to that of the classical PUs. However, alcohol is generated as a stoichiometric co-product in the reaction, making downstream separation steps necessary. Thus, to achieve high conversion and degree of polymerization, it is necessary to apply *in situ* vacuum distillation of the alcohol and use solvents.⁴⁷ Moreover, organocatalysts such as TBD (triazabicyclo-



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The emphasis is on replacing petrochemicals with bio-derived precursors and sustainable fillers such as industrial waste and natural powders. He explores non-isocyanate polyurethane (NIPU) foams, green recycling, and foamed concrete with reduced cement. He also investigates on graphene-based materials for enhancing functional properties in polymers and ceramics, aligning with the circular economy and sustainable innovation principles.



Martino Di Serio

Prof. Dr Martino Di Serio, PhD is a Full Professor of Industrial Chemistry at the University of Naples Federico II. His main research activities deal with the synthesis of novel products for biorefinery processes, with special attention to both kinetic and catalytic aspects of the investigated reactions. He is the author of 304 international publications with an H-Index of 47 (Scopus source, 06-04.2025).



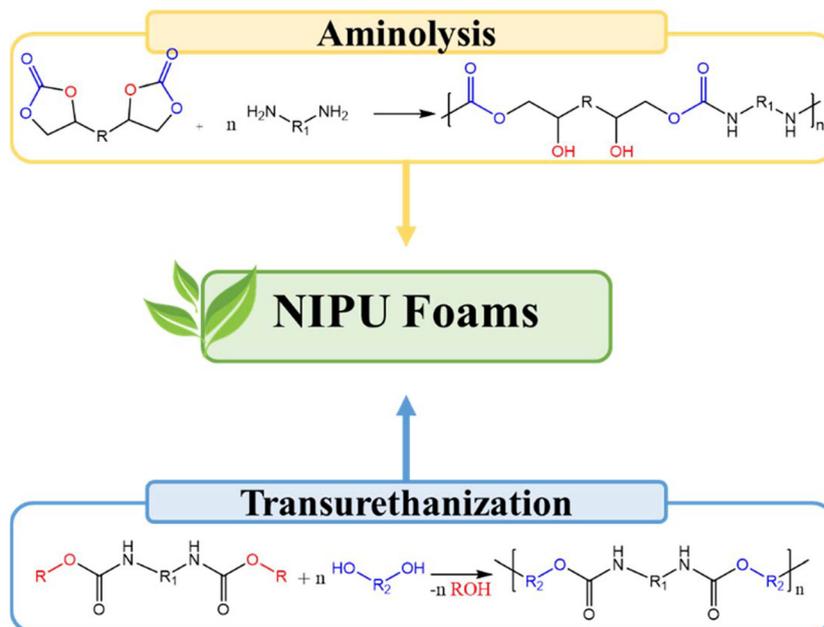


Fig. 1 Aminolysis and transurethanization as the two most promising eco-friendly routes for the synthesis of NIPU foams.

decene) are usually selected and the operating temperatures should exceed $110\text{ }^\circ\text{C}$ (ref. 47) for longer reaction times.

Besides the above-mentioned reactions, other isocyanate-free routes have been investigated such as the copolymerization of aziridine with carbon dioxide, the ring-opening polymerization of cyclic carbamates, and the reaction between carbamates and aldehydes (not reviewed herein).^{31,48} These routes have previously been deeply discussed in similar reviews on this topic,

and principally all promising. However, they still involve the use of toxic components *i.e.*, aziridines, aldehydes, and ethyl chloroformate, and have not been studied in the application of PU foams. Therefore, they will not be reviewed herein.

Blowing of NIPU can be performed by either physical or chemical blowing agents,^{49,50} *i.e.* non-self-blowing or self-blowing routes (*in situ* CO_2 formation), involving the decarboxylation of CCs by either hydrolysis,⁵¹ Pearson reaction between



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Vincenzo Russo

Prof. Dr Vincenzo Russo, PhD, TkD is an Associate Professor of Industrial Chemistry at the University of Naples Federico II, holding a PhD in Chemical Sciences and a second PhD in Chemical Reaction Engineering. His main research activities deal with kinetic and reactor modeling for biorefinery and water treatment processes. He is an expert in kinetic investigations based on reaction mechanisms and the design of multiphase

chemical reactors via multidimensional models. A special focus of his research activity is finding new synthetic paths to produce monomers for NIPU synthesis via the cyclocarbonation of epoxidized compounds. He is the author of 183 international publications with an H-Index of 28 (Scopus source, 06-04.2025).



CCs and thiols^{45,52,53} (*i.e.*, *S*-alkylation) and using amine/CO₂ adducts.⁵⁴ The type and concentration¹² of precursors and additives, *i.e.*, epoxy cross-linkers,⁵⁵ catalysts, and micro-/nano-sized fillers,⁵⁶ dictate the morphology of the cellular materials (*i.e.*, open/closed cell content, anisotropy, and apparent density) and influence their functional properties. All these parameters can be adjusted to tailor the final characteristics of NIPU foams and make them flexible or rigid materials depending on the final application. Similar to conventional PUs, flexible NIPU foams have open interconnected cell structures with viscoelastic properties, which can be applied in the automotive, cushioning/bedding, and biomedical sectors.¹⁴ Rigid NIPU foams have a closed cell morphology, resulting in good insulating materials⁵⁷ with excellent mechanical characteristics (high stress and impacts). Semi-rigid/semi-flexible foams share the characteristics of both categories and may have potential applications in several sectors, *i.e.*, automotive (*e.g.* integral skin foams), packaging, and building (spray foams). Fig. 2 displays the morphology, properties, and possible final applications where NIPU foams can replace conventional foams. In comparison with traditional PU materials, NIPU and NIPTU foams have intriguing peculiarities associated with the presence of pending OH or SH functional groups on their polymeric backbone, which play a crucial role in promoting the reprocessability of these materials.³²

The recent advances in the synthesis of NIPU foams are described in this review by examining the sustainable routes to obtain the building blocks of the foam precursors. A comprehensive overview on the synthesis of NIPU foams and sustainability aspects such as reprocessability through dynamic chem-

istry and recycling of these materials, mainly through chemical routes, as well as their environmental assessment, is provided and future developments are illustrated.

2. NIPU precursors

The agricultural waste from agro-industries, crop residues, and livestock is approximately 2 billion tons per year.⁵⁸ Thus, the valorization of this huge amount of biomass is extremely crucial from the viewpoint of a circular economy. Lignin, cellulose, organic acids, and vegetable oils can be extracted by the decomposition and further treatment of biomass and utilized as a feedstock for the production of added-value products,⁵⁹ such as biopolymers. Different strategies for the synthesis of natural-source monomers for NIPU foam precursors are discussed in the following sections.

2.1 Carbon dioxide

Since the beginning of the 21st century, greenhouse gas (GHG) emissions have shown a continuous upward trend. In particular, carbon dioxide (CO₂) emissions from emerging economies have become a dominant contributor, accounting for approximately 74% of the total global emissions in 2023. According to the latest Emissions Database for Global Atmospheric Research (EDGAR) report (2024), the global GHG emissions reached 994 million tonnes of CO₂ equivalent 994 (Mt CO_{2eq}) in 2023, an increase of 1.9% compared to the previous year.⁶⁰ This steady rise highlights the urgent need for effective climate mitigation

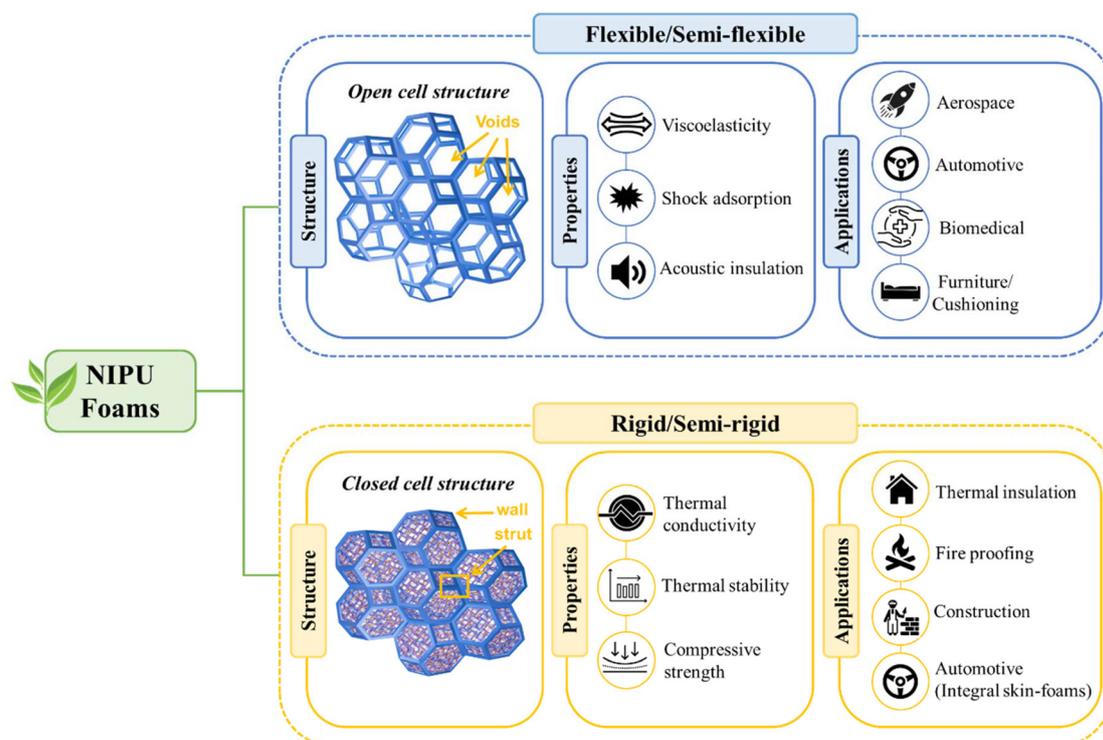


Fig. 2 NIPU foams: morphological characteristics, properties, and possible applications.



strategies. In response to regulatory pressure and growing environmental awareness, several major chemical companies have committed to significantly reducing their CO₂ emissions, with the long-term goals of achieving net-zero emissions by 2050. These initiatives reflect a broader industrial shift towards sustainability and innovation in carbon management practices, aligned with the objectives of the Paris Agreement.⁶¹

The most promising solutions are carbon capture and storage (CCS) and carbon capture and utilization (CCU) technologies, which aim to remove CO₂ from the atmosphere and either store it securely or convert it into useful products, respectively.^{42,62} CCS focuses on permanent storage, whereas CCU offers a pathway to transform captured carbon into fuels, chemicals, and materials, effectively closing the carbon loop. Importantly, the utilization of carbon dioxide as a chemical feedstock is not a recent innovation. As early as 1921, the industrial production of urea from CO₂ and ammonia was developed, which remains widely used in the fertilizer industry today.⁴² Additionally, CO₂ can be utilized in the dry reforming of methane, a process that converts CO₂ and CH₄ into synthesis gas (a mixture of H₂ and CO), which serves as a precursor for various fuels and chemicals in the energy sector. Another interesting decarbonization pathway is CO₂ conversion into cyclic carbonates and carbamates, which are the main precursors of isocyanate-free polyurethanes, as discussed in Section 2.2 and 2.3, respectively.

These examples demonstrate the diverse potential of CO₂ as a chemical building block. As technologies mature and economic incentives grow, CCU is expected to play a vital role in industrial decarbonization and the transition to a more circular, low-carbon economy.

2.2 Cyclic and linear carbonates

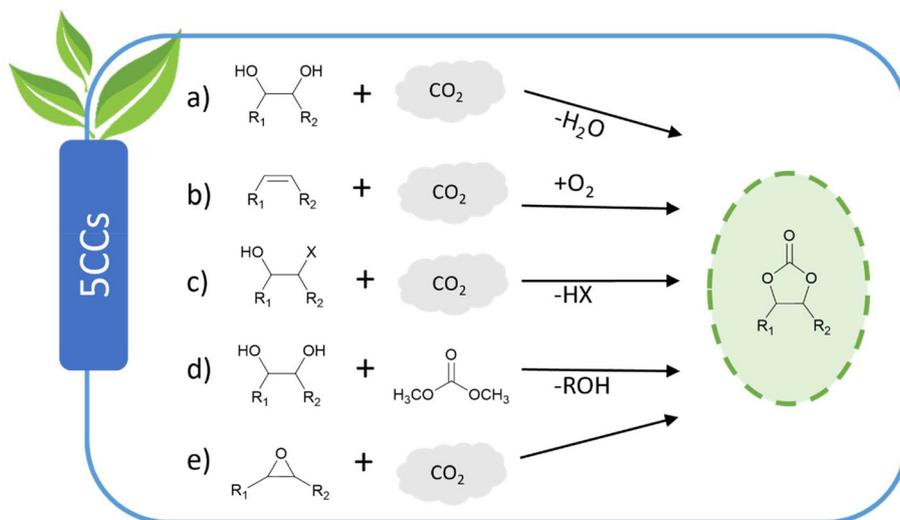
2.2.1 5-Membered cyclic carbonates (5CC). Undoubtedly, CCs represent the most prominent class of precursors for

NIPUs. Not only they can be generated by many natural substrates such as vegetable oils and terpenes,^{63–66} but also *via* different reaction pathways.³⁶ In 1957, Groszos & Drechsel⁶⁷ discovered polyhydroxyurethanes from cyclic carbonates and diamines. Subsequently, the research on this topic has expanded. Atmospheric CO₂ is employed as a co-reactant, which is particularly beneficial from an environmental viewpoint.^{68,69}

5CCs are mainly obtained *via* the cyclo-carbonation of diols (a),^{70,71} oxidative carboxylation of alkenes (b),⁷² the reaction of CO₂ and halohydrins (c),⁷³ (d) transcarbonation of diols with linear dialkyl carbonates and (e) cycloaddition reaction of CO₂ and epoxides,^{74–77} as illustrated in Scheme 2.

The cyclo-carbonation of diols (Scheme 2a) is exceptionally environmentally friendly given that diols can be obtained through the direct treatment of biomass; however, this reaction is hindered by both thermodynamics and kinetics, resulting in a very low yield of cyclic carbonates.^{78,79} The oxidative carboxylation of olefins (Scheme 2b) allows the one-pot synthesis of cyclic carbonates *via* the formation of an epoxy intermediate;⁸⁰ however, to the best of our knowledge, it has never been verified with greener substrates.

The reaction of CO₂ and halohydrins (Scheme 2c) can give a relatively high yield of 5CCs,⁸¹ but halohydrins are not abundant and halogen acids are inevitably produced as co-products. Another approach is the transcarbonation of diols with short-chained linear carbonates, *i.e.*, dimethyl and diethyl carbonates (DMC and DEC, respectively, Scheme 2d). It is an interesting alternative pathway to synthesize short-chain CCs. In this case, green reactants and mild operating conditions are usually employed.^{42,48} However, this route has been mainly studied for low molecular weight substrates, and the formation of methanol as a co-product of the reaction makes further separation steps necessary.^{32,82,83} Among the pathways presented, the cyclo-



Scheme 2 Most common routes used for the synthesis of 5CCs: (a) cyclo-carbonation of diols, (b) oxidative carboxylation of alkenes, (c) reaction of CO₂ and halohydrins, (d) transcarbonation of diols with dialkyl carbonates and (e) cycloaddition of CO₂ to epoxides.



addition of CO₂ to epoxides (Scheme 2e) is the most studied. Although it usually needs high temperatures and pressures, it involves the use of CO₂ as the reactant and registers 100% atom economy, generating high yields of cyclic carbonates without the formation of any stoichiometric coproducts.⁸⁴ Considering all the advantages and disadvantages of the reaction routes presented, the carboxylation of diols with dialkyl carbonates (d), and particularly the fixation of carbon dioxide to epoxides (e) are at the moment considered the most promising sustainable pathways because of their feasibility and versatility.⁸⁵

A broad spectrum of starting bio-based and waste-based materials can be used.⁸⁶ Namely, 5CCs have been successfully synthesized from vegetable oils,^{87–89} vanillin,⁹⁰ lignocellulosic biomass derivatives, *e.g.* diphenolic acid,⁹¹ and terpenes (*i.e.*, limonene).⁹² In the last few decades, the scientific community has focused on the development of homogeneous as well as heterogeneous catalysts to enhance the reaction rate and the selectivity towards carbonates, while operating under milder temperature and pressure conditions.⁹³ To catalyze epoxy ring opening, organic catalysts such as halide quaternary ammonium salts, *e.g.*, tetrabutylammonium bromide, iodide, and chloride (TBAB, TBAI, and TBAC), are usually utilized, and eventually combined with hydrogen-bond donors (HBD).^{94,95} HBD are compounds either with OH moieties, metals, or their combination, which act as Lewis acids, making the epoxy ring more prone to nucleophilic attack from Lewis bases. The halide ions, *i.e.*, Cl[−], Br[−] and I[−], in TBAX, usually act as Lewis bases, finalizing oxirane ring breakage.⁹⁵

Regarding the transcarbonation of diols, nucleophilic organocatalysts are usually employed such as cyclic amines, *e.g.*, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD); however, ionic liquids, molecular sieves, and metal oxides have also been demonstrated to act as selective catalysts for the carbonation of diols to cyclic carbonates.^{48,83}

Considerable effort has been made in the application of CCs for the synthesis of NIPU foams.¹³ Specifically, CCs with a functionality equal to or exceeding 2 are preferably applied as monomers for the synthesis of NIPUs with sufficiently high molecular weights. Table 1 presents the double or higher functionalized 5CCs successfully employed as monomers for the synthesis of NIPU foams, together with their molecular structures, raw materials, and synthesis process.

Bis-cyclic carbonates, *i.e.*, containing two cyclic carbonate functionalities, are the most common CCs, which have been synthesized using several alternative renewable sources. One of the first approaches was to introduce renewable epoxies in fossil-based epoxies to increase the bio-based content of the final product but maintaining most of the properties of the traditional products. For instance, a commercial mixture of 1,4-butanediol diglycidyl ether (bio-based) and the diglycidyl ether of bisphenol A, *i.e.*, DGEBA (fossil-based) named SR GreenPoxy 33 (Sicomino epoxy systems), was successfully converted to the respective 5CCs using atmospheric CO₂ at 105 °C and promoted by TBAB.⁵⁵

Cashew nutshell liquid (CNSL) has been recently explored as a raw material for the synthesis of bis-cyclic carbonate pre-

cursors. CNSL is an interesting biowaste material given that it is rich in phenolic derivatives, *i.e.* anacardic acid and cardol, which can be converted into valuable cardanol.⁹⁶ After further treatment, cardanol can be functionalized into many compounds. The Cardolite company produces a cardanol-based diepoxy named Cardolite® NC-514, which has been employed as a starting material in the synthesis of cyclic carbonates by the group of Torkelson.^{45,97} The complete conversion of cardanol diepoxy into the respective bis-cyclic carbonate was registered after 80 h of reaction at 80 °C and in the presence of dimethylformamide (DMF) as a solvent.⁹⁸ The final product was utilized for the synthesis of NIPU foams after the separation of the solvent.

Another interesting source of NIPU foam precursors is lignin and its derivatives. Lignin is a widely abundant biopolymer with a complex chemical structure and rich in phenolic hydroxy functional groups. Kraft lignin, which is a type of lignin obtained from the waste of the pulp and paper industries, has been converted into cyclocarbonated lignin in a two-step process involving oxyalkylation with glycerol carbonate (GC), followed by transesterification with dimethylcarbonate (DMC) in DMSO (dimethyl sulfoxide).⁹⁹ As a result, the lignin-based bis-cyclic carbonate was found to have exceptionally high reactivity towards diamines. However, the yield of oxyalkylated lignin in the first reaction was below 10% due to side reactions. Unfortunately, lignin is difficult to handle due to its very low solubility and brittleness, high-temperature sensitivity, and heterogeneity. Therefore, future research on this process is necessary to overcome these limits.

Besides lignin, its phenolic derivatives can be employed in the synthesis of 5CCs. For instance, a very interesting product of lignin depolymerization, *i.e.*, resorcinol, can be coupled with CO₂ at 12 bar after being functionalized with epichlorohydrin.¹⁰⁰ The resulting 5-membered bis-cyclocarbonate can be used as a monomer for the synthesis of NIPHU foams. The synthesis of bis-cyclic carbonates from sugars has also been reported. For instance, sorbitol is a very promising bio-based building block for the synthesis of fossil-free polymeric materials. Sorbitol-based CCs¹⁰¹ have been prepared starting from sorbitol and dimethyl carbonate, and successfully employed as co-monomers of diamines in the preparation of flexible NIPU foams.

Multifunctional cyclic carbonates, with functionalities higher than 2, are particularly interesting, given that they enable the creation of highly crosslinked, isocyanate-free polyurethane foams. Compared to bifunctional monomers, they donate higher cross-linking density to the final material given that the other cyclocarbonate moieties act as cross-linkers between the polymer chains. An example of multifunctional cyclic carbonates is trimethylolpropane triglycidyl carbonate (TMPTC), which is obtained from trimethylolpropane by functionalization with epichlorohydrin, followed by coupling with CO₂. TMPTC has three cyclic carbonate functionalities and can be either used in copolymerization with diamines⁵¹ or further ethoxylated into a TMPTC derivative (EO-TMPGC). Blattman *et al.*⁵⁰ selected a blend of these carbonates in the





Table 1 Sustainable cyclic carbonates employed in the synthesis of NIPU foams: reaction conditions, chemical properties, and raw materials

Chemical properties of the CCs		Reaction conditions					CCs			
Substrate	Structure	Raw material	CC functionality	T (°C)	P (bar)	Reaction time (h)	Catalyst	Solvent	Yield (%)	Ref.
Soybean oil cyclic carbonate		Soybean oil	>2	100	100	10	TBAB + HBD	—	100	Grignard <i>et al.</i> ¹⁰³
Poly(ethylene glycol) biscarbonate		PEG	2	80	10	0.6	TBAI + HBD	—	100	Grignard <i>et al.</i> ¹⁰³
Cyclic carbonate of resorcinol diglycidyl ether (RDGCC)		Resorcinol	2	—	12	12	—	—	97	Clark <i>et al.</i> ¹⁰¹
Glycerol polyglycidyl carbonate		Glycerol	3	110	90	24	TBAI	—	>98	Blattman <i>et al.</i> ⁵⁰
Sorbitan bis-carbonate		Sorbitol	2	80	—	24	K ₂ CO ₃	MeOH	40	Clark <i>et al.</i> ¹⁰¹



Table 1 (Contd.)

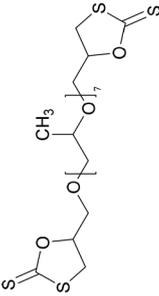
Substrate	Structure	Raw material	CC functionality	Reaction conditions					CCs Yield (%)	Ref.
				T (°C)	P (bar)	Reaction time (h)	Catalyst	Solvent		
Cyclocarbonated lignin		Lignin	—	75	—	4	K ₂ CO ₃	GC/ DMSO	96–98	Sternberg and Pilla ³⁹
Trimethylol-propane triglycidyl carbonate (TMPTC)		Trimethylol propane	2.6	110	90	24	TBAI	—	>8	Blattman <i>et al.</i> ⁵⁰ Purwanto <i>et al.</i> ⁹⁷
Poly(propylene oxide) bis-carbonate (PPOBC)		PPO	2	80	15	36	LiBr	DMF	76	Purwanto <i>et al.</i> ⁹⁷
Ethoxylated TMPTC (EO-TMPTC)		Trimethylol propane	3	140	10	96	TBAB	—	100	Blattman <i>et al.</i> ⁵⁰



Table 1 (Contd.)

Substrate	Structure	Raw material	CC functionality	Reaction conditions					CCs Yield (%)	Ref.
				T (°C)	P (bar)	Reaction time (h)	Catalyst	Solvent		
Cardolite® NC-514 cyclic carbonate		Cashew nutshell liquid	2	80	—	80	TBAI	DMF	100	Purwanto <i>et al.</i> , ⁴⁵
Linseed oil cyclic carbonate		Linseed oil	>2	120	60	12	TBAB	—	79	Wang <i>et al.</i> , ⁸⁵
TC6		Trimethylol propane allyl ether	4	60	1	16	AIBN	1,4-Dioxane	87	Coste <i>et al.</i> , ¹⁰⁷
SR GreenPoxy 33 cyclic carbonate		SR GreenPoxy (mixture of DGEBA and 1,4-butanediol diglycidyl ether)	>2	105	1	12	TBAB	—	85	Chaib <i>et al.</i> , ⁵⁵

Table 1 (Contd.)

Substrate	Structure	Raw material	CC functionality	Reaction conditions					CCs Yield (%)	Ref.
				T (°C)	P (bar)	Reaction time (h)	Catalyst	Solvent		
Polypropylene oxide bis-thiocarbonate (PPOTC)		PPO	2	60	1	96	LiBr	EtOAc	85	Coste <i>et al.</i> , ¹⁰⁷

synthesis of NIPU foams to tailor the structure and properties of the final material. According to the authors, blending TMPTC with EO-TMPGC resulted in higher flexibility of the polymeric matrix owing to the longer ether chains of EO-TMPGC. The possibility to blend different cyclic carbonates has also been explored by other research groups. Cornille *et al.* first synthesized TMPGC and a polypropylene oxide bis-carbonate (PPOBC) by coupling CO₂ to the respective tri- and di-glycidyl ethers.¹⁰² They prepared different blends of TMPGC and PPOBC, investigating the effect of the CC formulations on the characteristics of the final material in the aminolysis process. More recently, Bourguignon *et al.*⁵³ synthesized a new glycerol-based trifunctional 5CC from CO₂ and bio-based glycerol triglycidylether. As a result, employing this 5CC in the synthesis of NIPU foams rather than TMPTC endowed the final material with a higher bio-based content (up to 90%).⁵³

Cyclic carbonates with a functionality exceeding 3 can be obtained from epoxidized vegetable oils. The possibility of employing vegetable oils as a source of NIPU foam precursors has indeed been explored by some research groups. For instance, the carbonation of linseed oil epoxy was carried out under solvent-free conditions at 60 bar and 120 °C in the presence of TBAB, resulting in highly functionalized monomers for the synthesis of NIPU foams.⁸⁹ Grignard *et al.* produced soybean oil cyclic carbonates by coupling CO₂ with epoxidized soybean oil (ESBO) at 100 bar and 100 °C and employing a bifunctional catalytic system of TBAB with 1,3-bis(hydroxyhexafluoroisopropyl)benzene as a hydrogen bond donor.

The carbonation of ESBO was compared with that of a bifunctional epoxy compound, *i.e.*, poly(ethylene glycol) diglycidyl ether. As a result, the reactivity of the compound containing terminal epoxy groups was higher given that shorter reaction times were observed under milder operating conditions, *i.e.*, at a 10-times lower pressure. A similar trend of the reactivity was translated to the carbonation products in the aminolysis process to obtain NIPU foams.¹⁰³ Hence, multifunctional cyclic carbonates are valuable monomers in the synthesis of highly cross-linked NIPU foams; however, the carbonation rate of these compounds is lower compared to bifunctional carbonates because the internal epoxy groups are more sterically hindered than the terminal groups.

As demonstrated by the above-mentioned studies, replacing toxic monomers with bio-based cyclic carbonates as monomers for NIPU foams is not only feasible but already shown to be possible. The diversity of renewable/waste sources that can be employed in the synthesis of CCs is a great advantage given that it does not limit the production of CCs to a single feed-stock. Moreover, CCs can be obtained in most cases under solvent-free conditions in very high yields, and thus no additional separation steps are required.

To date, very few techno-economic assessments have been conducted exclusively focusing on low molecular weight cyclic carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC).¹⁰⁴ The main challenges identified include the need for high pressures, the cost and availability of the starting materials. However, the price of the final CCs can become



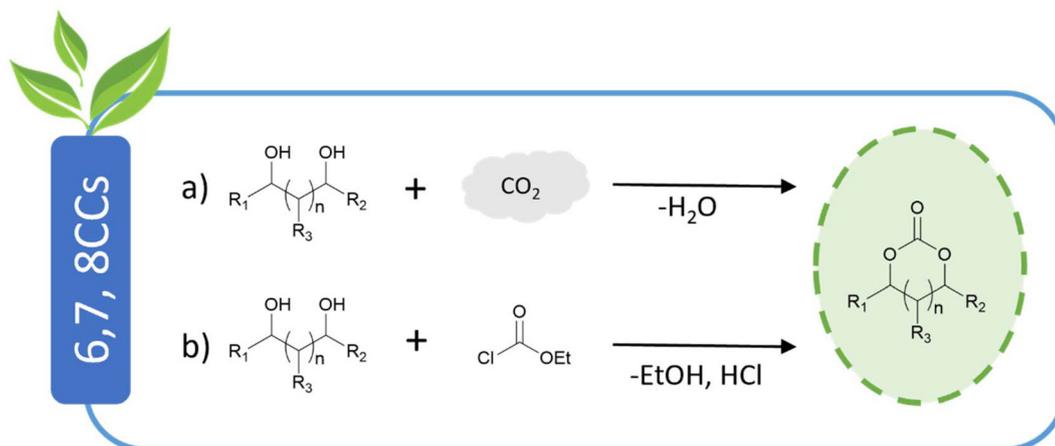
more competitive in the future, especially considering the savings on CO₂ taxes that the plant can achieve by utilizing CO₂ as a feedstock, as pointed out by Mishra and Peter.¹⁰⁵ The Life Cycle Assessment (LCA) of ethylene carbonate production from coupling CO₂ to epoxide was demonstrated to be more environmentally friendly compared to the traditional routes. Moreover, employing CO₂ as a raw material is economically beneficial given that it is widely available and inexpensive. The main disadvantages are the relatively high pressures and temperatures employed, which increase the overall process cost.¹⁰⁶ Also, Pescarmona⁹⁵ emphasized that employing CO₂ in the synthesis of cyclic carbonates cannot counterbalance anthropogenic carbon dioxide emissions alone because of the large gap between the latter and the actual annual production of 5CCs. Another important point is that all the cyclic carbonates presented were obtained employing discontinuous processes, which are generally not the most convenient on an industrial scale. To date, the continuous approaches, *e.g.*, microreactors and tubular reactors, have been mainly applied for the carbonylation of low-molecular-weight monofunctional epoxides, *e.g.* ethylene oxide, 1,2-epoxyoctane, and styrene oxide⁹² but not other more complex bio-based systems.⁸⁵

2.2.2 6-, 7- and 8-membered cyclic carbonates. Although five-membered cyclic carbonates are the most common monomers, larger CC rings, *i.e.*, six-, seven- and eight-membered CCs have also been explored. According to many authors, they are valuable precursors of NIPU given that they are more reactive than 5CCs in the reaction with diamines. In particular, the rate constants of their aminolysis with different amines, *i.e.*, hexylamine and benzylamine, increase by approximately one order of magnitude per number of carbon atoms introduced in the carbonate ring (5CCs < 6CCs < 7CCs).^{46,105} In the case of 5CCs, 6-, 7-, and 8-CCs are traditionally obtained from phosgene derivatives. For instance, six- and seven-membered cyclic carbonates with double functionality were synthesized by Tomita *et al.*¹⁰⁸ by reacting the harmful triphosgene with either a 1,3-diol or 1,4-diol, respectively.

Nevertheless, different phosgene-free routes have been proposed as promising alternatives in the last decade. The possibility of coupling CO₂ with 1,3-diols is undoubtedly the most attractive in terms of sustainability (Scheme 3a). Generally, this reaction is carried out in the presence of a solvent, *i.e.*, chloroform and acetonitrile, at relatively low temperatures and pressures, catalyzed by mild and strong bases, and eventually combined with a dehydrating agent when the base is moisture sensitive.⁷¹ The first example of the base-catalyzed cyclocarbonation of diols is the work by McGuire *et al.*⁷¹ In particular, 6-, 7- and 8-membered CCs with one carbonate functionality were synthesized from different diols and CO₂ at mild temperatures and pressures. High conversions of diols were achieved, whereas the yields of the resulting 6, 7, and 8 CCs were 71%, 61%, and 43%, respectively, due to side reactions.

Another possibility is to combine diols with ethyl chloroformate (Scheme 3b). For instance, bis-6CCs were prepared starting from castor oil-derived methyl 10-undecenoate through a four-step process.¹⁰⁹ In particular, in the second step, undecenoate 1,3-diol is produced and reacts with ethyl chloroformate to obtain the respective 6CCs. To increase the CC functionality, dimerization of the 6CCs was carried out; as a result, the undecenoate bis-6-membered CC was obtained. Finally, the authors compared the aminolysis kinetics of the 6CCs and the equivalent 5-membered CCs. Again, the former monomer was more prone to react with amines. However, the synthesis of these monomers involves many steps and the use of solvents *i.e.*, DMF, tetrahydrofuran (THF), and pentane. Moreover, the conversion of the reactants and the yields of the main products of each step are below unity, and thus separation steps between the process steps are required.

Despite the positive results, the high ring strain and instability of the larger CC rings promote side reactions, impairing the selectivity for the aminolysis main product. Compared to their 5-membered counterparts, high yields of larger CC rings are indeed less likely achieved, which is the main drawback of their eventual upscaling.⁶⁹ Thus, their appli-



Scheme 3 Main routes for the synthesis of 6,7 and 8 CCs: (a) cyclocarbonation of diols and (b) reaction of diols with chloroformate.



cation in the synthesis of NIPU is still limited. To the best of our knowledge, only one research article has been published regarding the synthesis of NIPU foams with 6-membered CCs from phosgene-free sources,¹¹⁰ while no scientific report employing 7 or 8 CCs to produce NIPU foams was recorded, suggesting the infancy of research in this field.

2.2.3 Cyclic thiocarbonates. The employment of sulfur compounds, *e.g.*, thiols, as additives in the formulation of cyclic carbonates and diamines is well known to be particularly advantageous, significantly accelerating the decarboxylation of 5CCs. The *S*-alkylation of 5CCs releases CO₂ *in situ* via the Pearson reaction, thereby enhancing the overall efficiency and rate of NIPU foam synthesis.^{45,52,89} A relatively new approach in the field of NIPU precursors is the use of thiol derivatives of cyclic carbonates, *i.e.*, cyclic thiocarbonates (CTCs).¹¹¹ They have attracted particular attention as potential monomers and co-monomers in the production of NIPU foams given that their reactivity towards diamines is higher than their traditional counterparts. When employing a mixture of 5CCs and CTC, a domino of three reactions occurs, *i.e.*, the aminolysis of CTCs, producing a thiol derivative, which then reacts with the 5CC through *S*-alkylation, generating CO₂, and finally the aminolysis of 5CC.¹⁰⁷ For instance, Monie *et al.* utilized a particular CTC, *i.e.*, *N*-acetylhomocysteine thiolactone, as the *latent thiol* together with a CC and diamine to produce NIPU foams through a series of consecutive reactions.⁵² According to the authors, this *one-pot* approach is highly advantageous given that the reactivity of the thiolactone towards diamines is very high, reducing the reaction times needed in the aminolysis of traditional CCs. Moreover, in this way, the aid of blowing agents is avoided given that CO₂ is produced *in situ* from the *S*-alkylation of the CC by the thiol intermediate.

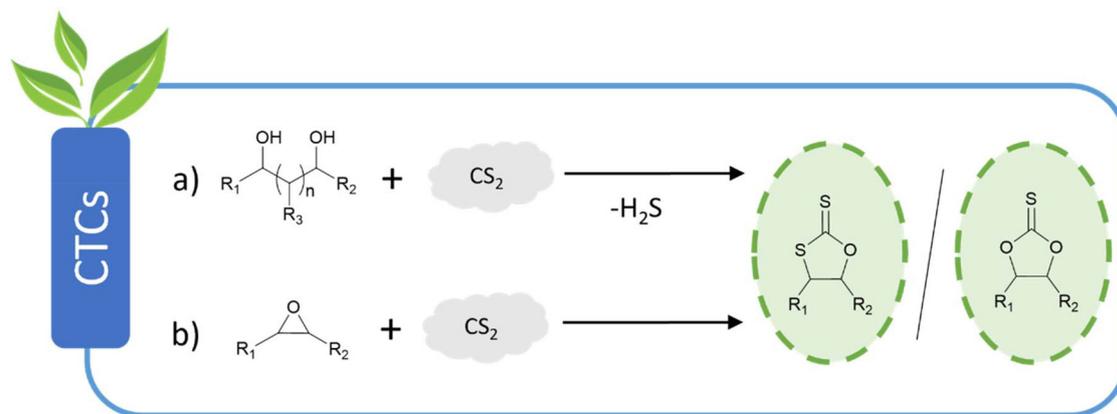
Similar to traditional CCs, CTCs can be synthesized using diols and the harmful (thio)phosgene.⁴⁶ Alternatively, CTCs can be obtained by the reaction between either diols or epoxides (Scheme 4b) with carbon disulfide (CS₂), *i.e.*, a gaseous by-product from the fiber industry.¹¹¹

Given that the reactivity of substrates with CS₂ is higher than CO₂, milder reaction conditions, *i.e.*, room temperature and short reaction times, are usually sufficient to get high yields of CTCs. Depending on the starting material, catalyst, solvent, and operating conditions, cyclic mono- or di-thiocarbonates can be synthesized (Scheme 4). In case (a) (Scheme 4), one sulfur atom is present in the cyclic structure in place of oxygen, whereas in case (b), two sulfur atoms replace two oxygen atoms, respectively. Under specific reaction conditions, *e.g.*, high temperature and in the presence of protic and highly polar solvents, cyclic trithiocarbonates and episulfide can be produced as by-products.¹¹² The choice of the oxirane substrate influences the selectivity of the main products. In fact, the reaction of glycidyl phenyl ether with CS₂ in THF at room temperature and catalyzed by the alkali metal halide LiBr yields 97% of the corresponding five-membered cyclic dithiocarbonate in 4.5 h of reaction. However, when employing different epoxides such as vicinal disubstituted epoxides, the yield of the cyclic dithiocarbonates is lower, and longer reaction times are needed.¹¹³

Recently, Coste *et al.* synthesized a thiocarbonate with a double functionality by reacting poly(propylene oxide) diglycidyl ether and carbon disulfide for 96 h at 60 °C and in the presence of LiBr as a homogeneous catalyst. Under these conditions, the thiocarbonation reaction resulted in the formation of a cyclic di-thiocarbonate with a yield of up to 85%.^{46,107}

However, despite the highly interesting properties of CTCs as possible alternatives to CCs, academic research has mainly been focused on the latter subject, as proven by the huge gap in the number of publications on CTCs compared to that of CCs. In fact, in the period 1990–2024, only 1141 articles were published on cyclic thio- and dithio-carbonates, whereas 107 854 articles were published on traditional cyclic carbonates (Scopus, Keywords: cyclic dithiocarbonates OR cyclic thiocarbonates, cyclic carbonates, October 2024).

2.2.4 Linear/acyclic carbonates (LCs). Short-chained dialkyl carbonates such as dimethyl and ethyl carbonates (DMC and DEC, respectively) are extremely versatile chemicals that can be



Scheme 4 Main phosgene-free routes for the synthesis of cyclic thiocarbonates (CTCs): cycloaddition of carbon disulfide to (a) diols and (b) epoxides.



employed as intermediates in many different processes. Moreover, they are considered non-toxic *green* chemicals given that they are nowadays obtained *via* phosgene-free routes. As discussed in Section 2.1.1, short-chained dialkyl carbonates are particularly interesting building blocks for the production of 5CCs through the transcuration reaction of diols (Scheme 2e).¹¹⁴ When further functionalized, they can also be employed in the synthesis of long-chain linear carbonates (LCs), which have appeared as valid alternatives to their cyclic counterparts as monomers in the synthesis of NIPUs. To achieve sufficient molecular weights, DMC or DEC are usually reacted with alcohols with functionality equal to or higher than 2 (Scheme 5). The transesterification of dialkyl carbonates with hydroxy functionalities produces suitable linear carbonate monomers for polymerization with diamines to obtain NIPU materials.¹¹⁵

Among the dialkyl carbonates, dimethyl carbonate (DMC) is the most utilized for this purpose, given that it is the most prone to nucleophilic substitution.¹¹⁶ The carboxymethylation reaction is usually carried out at a relatively mild temperature and using an organic solvent. Depending on the operating conditions and catalyst used, a mixture of linear and cyclic carbonates might be obtained.⁸⁰ Besides alcohols, tannins, lignin, and sugars have recently appeared as alternative sources of hydroxyl groups in the transcuration with DMC.¹¹⁷

For instance, the carboxymethylation of glucose with DMC was reported by Xi *et al.*,¹¹⁸ who conducted the reaction in an aqueous environment at 50 °C for 40 min. As a result, a bio-based carbonate monomer was obtained, and then further reacted with diamines to generate urethane bonds for the synthesis of NIPU foams.¹¹⁵ Under similar synthetic conditions, the transcuration of tannins with DMC was carried out, demonstrating the feasibility of this reaction with different renewable sources. The tannin-based carbonate was utilized for the synthesis of NIPU foams.¹¹⁹

However, the lack of work utilizing the transcuration pathway to produce monomers for the synthesis of NIPU foams is surprising given that this route is relatively easy compared to that for obtaining cyclic carbonates. In fact, it proceeds at high reaction rates at low temperatures (below 90 °C) and it does not require any cyclization step.¹¹⁴ Conversely, it is

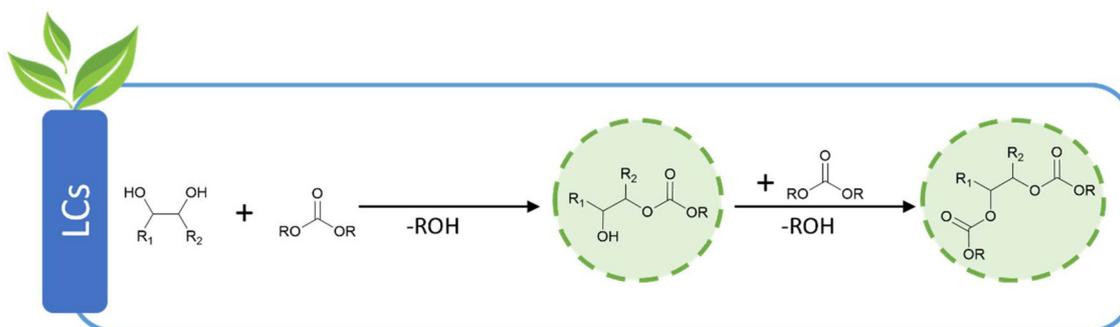
a relatively new approach given that the first article on this topic only appeared five years ago.¹¹⁷ Moreover, the polycondensation of linear carbonates with diamines produces alcohols as co-products that need to be separated compared to the polyaddition of cyclic carbonates with diamines, which yields only the isocyanate-free polyurethane unit.⁴⁸ Thus, considering all the reasons discussed, more research on the topic is expected to be carried out in the following years.

2.3 Carbamates

The catalyzed polycondensation of di-carbamates with either polyols or diamines is an alternative approach for the synthesis of NIPU materials.¹²⁰ In the case of isocyanates, carbamates have been traditionally synthesized from phosgene; however, more sustainable routes have been recently identified. For instance, Unverferth *et al.*⁴⁷ developed a novel method to synthesize dicarbamates from castor oil in five reaction steps. However, although this is an interesting sustainable approach, the high number of reactions and separation steps required may limit its feasibility on a large scale. Thus, the most promising phosgene-free processes for the synthesis of carbamates are illustrated in Scheme 6, *i.e.*, the reaction of urea or urea derivatives with alcohol (a), aminolysis of dialkyl carbonates (b) and carboxylation of amines with CO₂ and an alcohol (c).

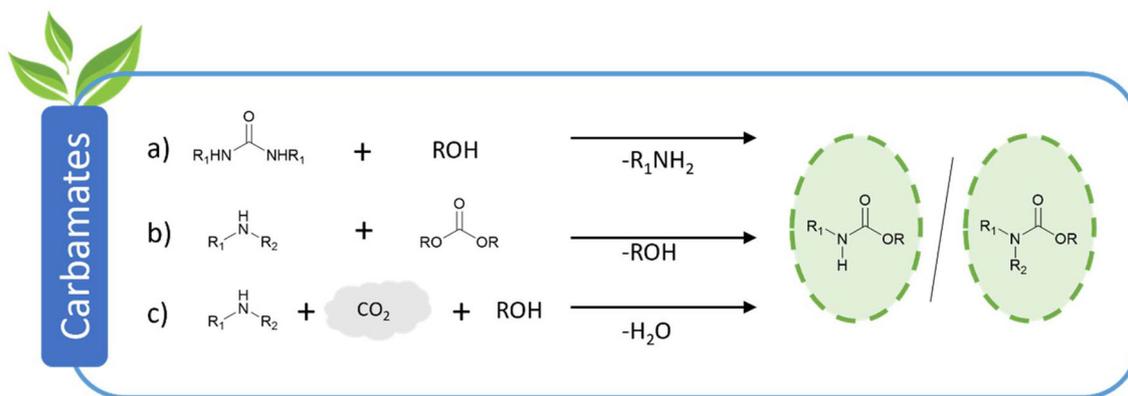
Phosgene-free pathways (a) and (b) in Scheme 6 to obtain carbamates are well-known, where the former is usually preferred to the latter from an economical point of view, given that the cost of urea is certainly lower than that of carbonates. However, urea is chemically more stable, and therefore less reactive than carbonates. Moreover, to the best of our knowledge, the alcoholysis of urea and urea derivatives has not been utilized to date for the production of monomers dedicated to the application of NIPU foams.

Pathway (b) is regarded as environmentally friendly given that it involves dialkyl carbonates such as DMC, which are considered green and safe chemicals, and diamines obtained, for example, through fermentation processes (Paragraph 2.3). Moreover, the reaction conditions are usually relatively mild, and the reaction rates quite rapid when employing a specific catalyst.^{121–123} A recent publication applied this pathway for the synthesis of carbamates by reacting DMC and hexamethyl-



Scheme 5 Transcuration of alcohols with dialkyl carbonates.





Scheme 6 Different phosgene-free pathways for the synthesis of carbamates: (a) alcoholysis of urea/urea derivatives, (b) aminolysis of dialkyl carbonates and (c) carboxylation of amines with CO₂ and an alcohol.

ene diamine for 1 h at 70 °C. The resulting carbamate was reacted with D-xylose as a bio-sourced alcohol to yield NIPU foams.¹²⁴ Similarly, dicarbamates were synthesized from DMC and Priamine 1074 for 5 h at 80 °C employing TBD as the catalyst. The same authors utilized the biscarbamate monomers further in the synthesis of NIPU foams through the transurethanization approach.¹²⁴

Particularly, the carboxylation of amines with CO₂ and an alcohol (c) is attractive from both an environmental and technological viewpoint.¹²⁵ This pathway is intriguing given that it involves the utilization of CO₂.¹²⁶ However, the formation of water as a co-product is a thermodynamic barrier in the reaction; therefore, dehydrating agents usually need to be employed as well as harsh temperature and pressure conditions, *e.g.*, up to 120 °C and 50 bar, respectively.^{127,128} Thus, to mitigate these issues, different approaches have been investigated. For instance, replacing alcohols with regenerable metal alkoxides was demonstrated not only to remove the need for dehydrating agents but also reduce the operating CO₂ pressure to 1 bar.¹²⁷ In the work by Zheng *et al.*,¹²⁸ aromatic carbamates were obtained under milder reaction conditions (60 °C and 10 bar) employing protonic ionic liquids both as catalysts and substrates and CH₂Br₂ as a solvent/dehydrating agent. The authors obtained a high amine conversion (97%) and selectivity to the desired carbamate product (99%), demonstrating the multiple recyclability of the catalyst as well. A similar approach that does not require the use of alcohols is the preparation of dicarbamates as amine-CO₂ adducts. Recently, Choong *et al.*⁵⁴ synthesized different adducts *via* the reaction between triethylenetetramine and CO₂ catalyzed by organic bases, *i.e.*, DBN. The resulting adducts were successfully utilized as co-monomers in the synthesis of NIPU foams. Another class of isocyanate-free carbamate monomers is the bis-carbonylimidazolides (BCI). They can be obtained from the reaction between a diol, *e.g.*, 1,4-butanediol, and carbonyldiimidazole in a relatively few steps and with a final yield exceeding 90%. BCI monomers can be particularly beneficial in the application of NIPU foams given that they spontaneously

release CO₂ at 140 °C, providing an *in situ* blowing effect. In fact, the reaction between BCI monomers and triamine resulted in the formation of flexible as well as rigid NIPU foams.¹²⁹ Despite the few examples available, the use of carbamates as monomers for the synthesis of NIPU foams through the transurethanization approach is highly interesting. Through this process, traditional urethane linkages are obtained, rather than the hydroxyurethane linkages obtained in the polyaddition of CCs with diamines. For this reason, the interest in this pathway may encourage the scientific community to conduct further research on the synthesis of sustainable carbamates and their use in the formulation of foamed polyurethane materials.

2.4 Diamines

Amines with a double primary amine moiety are usually utilized as co-monomers in the reaction with cyclic carbonates. The choice of a specific diamine is particularly crucial given that it can influence the kinetics of the polyaddition reaction with cyclic carbonates as well as the properties of the final material. Depending on the final application of the NIPU foams, either linear or cycloaliphatic diamines can be employed, while aromatic diamines are usually utilized for NIPU coatings and adhesives. For instance, linear aliphatic diamines can be more suitable to synthesize soft and flexible NIPU foams. However, the longer the carbon chain, the lower the reactivity of the diamine. Alternatively, cycloaliphatic diamines can provide rigidity, but also brittleness to the material.¹¹⁰

Diamines are traditionally produced from fossil-based substrates, *e.g.* propylene and butadiene. Owing to the recent cutting-edge advances in bio-engineering, diamines nowadays can be synthesized in more sustainable ways.¹³⁰ A recent review by Wang *et al.*¹³¹ described all the strategies for the bio-synthesis of both aliphatic and aromatic diamines in detail. However, aliphatic diamines are mainly selected for the synthesis of NIPU foams. In particular, the diamines discussed



hereafter together with their structure, bio-source, and production process are presented in Table 2.

Bio-based diamines with 3–5 carbon atoms in their backbone can be biotechnologically produced through the fermentation of biomass-derived sugars, *e.g.* glucose and xylose. In particular, 1,3-diaminopropane, putrescine (1,4-diaminobutane, DAB), cadaverine (1,4-diaminopentane, DAP), and spermidine (*N*¹-(3-aminopropyl)butane-1,4-diamine) can be obtained *via* the metabolic pathway of different bacteria such as *E. coli* and *C. glutamicum*,^{131,132} either naturally or synthetically with the aid of specific enzymes. Alternatively, bio-based 1,4-butandiamine can be obtained using biomass-derived succinic acid,¹³³ while cadaverine can be produced from the decarboxylation of L-lysine catalyzed by organocatalysts.^{43,101}

Sustainable pathways for the production of renewable longer-chain diamines have been reported in the literature. For instance, 1,10-decanediamine has been prepared by the chemical conversion of castor oil in a three-step process. In particular, castor oil-derived sebacic acid was first reacted with ammonia, followed by dehydration and catalytic hydrogenation steps.¹³⁴ Hexamethylenediamine (HMDA), also known as 1,4-hexanediamine,^{50,135} has also been successfully syn-

thesized from renewable feedstock such as starch.⁵⁰ In particular, starch-derived 5-hydroxymethylfurfural (HMF)¹³⁶ can be converted into HMDA through three different catalytic processes. Two possible routes are hydrogenation to 2,5-bis(hydroxymethyl)tetrahydrofuran (THFDM), followed by either amination and hydro-deoxygenation or hydrogenolysis and amination. Another possibility is the oxidation of HMF followed by reductive amination and hydrodeoxygenation.¹³⁷

Moreover, in 2013, the American company *Rennovia* developed new technology for the synthesis of renewable adipic acid-based HMDA.¹³⁸ Other vegetable oil-derived diamines are produced by Croda under the commercial name of Priamine™. Specifically, they are a class of cycloaliphatic diamines derived from fatty acid dimers¹²¹ and some of them, *i.e.*, Priamine™ 1073 and Priamine™ 1074, have been successfully employed in the synthesis of NIPU foams.^{49,138}

Another trend in the field of bio-monomers for aminolysis reactions is the utilization of amino acids. Employing amino acids as amines can be particularly beneficial from both an environmental and economical point of view given that they are natural and inexpensive feedstock, which can be produced by the fermentation of sugars.^{139,140} To date, L-lysine,

Table 2 Bio-based diamines employed in the synthesis of NIPU foams (readapted from Meyer *et al.*¹⁴⁰)

Substrate	Structure	Renewable building block	Process	Ref.
1,3-Diaminopropane (1,3-DAP)		Glucose	Fermentation of sugars with bacteria	Wang <i>et al.</i> ¹²⁷
1,4-Diaminobutane (1,4-DAB) or putrescine		Glucose	Fermentation of sugars with bacteria	Wang <i>et al.</i> ¹²⁷
1,5-Diaminopentane (1,5-DAP) or cadaverine		Succinic acid	Chemical conversion of succinic acid	Sen Choong <i>et al.</i> ⁵⁴
<i>N</i> ¹ -(3-Aminopropyl)butane-1,4-diamine or spermidine		Glucose	Fermentation of sugars with bacteria	Wang <i>et al.</i> ¹²⁷ Dros <i>et al.</i> ¹³⁷ Meyer <i>et al.</i> ¹⁴⁰ Dros <i>et al.</i> ¹³⁷
1,6-Diaminohexane		Starch	Chemical conversion of hydroxymethylfurfural to 1,6-butandiol, followed by high-pressure amination	Dros <i>et al.</i> ¹³⁷ Radzik <i>et al.</i> ¹³⁴
L-Lysine		Biomass L-Lysine	Hydrogenation of bio-adiponitrile Fermentation of sugars and ammonia with bacteria	Lee <i>et al.</i> ¹³⁶ Meyer <i>et al.</i> ¹⁴⁰ Booyesen <i>et al.</i> ¹⁴¹
1,10-Diaminodecane		Castor oil	Chemical conversion of castor oil	Sen Choong <i>et al.</i> ⁵⁴
Isophorone diamine (IPDA)		Bio-based acetone	Condensation of acetone followed by hydrocyanation and amination	/crosslinkers.evonik.com/en/ ¹⁴⁴
Cycloaliphatic diamines, priamine™		Fatty acids	Chemical conversion of fatty acids	https://www.cargill.com/bioindustrial/priamine ¹⁴³



L-glutamine, L-arginine, and L-asparagine have already been explored as natural amines in the reaction with cyclic carbonates to produce NIPU foams.¹⁴¹ The experiments employing L-glutamine, L-arginine, and L-asparagine did not result in the production of NIPU foams, given that heterogeneous mixtures of the amine and the cyclic carbonate were obtained, whereas the reactions with L-lysine successfully produced NIPU foams. According to the authors, the successful results with L-lysine can be explained by its higher solubility in the reaction mixture compared to the other amino acids, owing to its particular structure carrying a positive charge. Among the amino acids studied, L-lysine appears to be the most promising for the synthesis of isocyanate-free foams owing to the above-mentioned reasons, but also because for future scale-up, it is already available on the market in large amounts as a nutrition supplement.¹⁴¹

Cycloaliphatic diamines are interesting building blocks in the cycloaddition reaction with cyclic carbonates. In particular, they can offer more rigidity to the final material owing to their structure compared to linear diamines. Among the bio-based cycloaliphatic diamines, isophorone diamines (IPDA) are quite promising given that isophorone can be synthesized from bio-based acetone. In particular, the group of Caillol have already coinvestigated the potential use of isophorone diamine (IPDA) in the reaction with six-membered cyclic carbonates to produce rigid NIPU foams.¹¹⁰

Considering the wide variety of bio-based diamines presented, it is clear that both the academic and industrial communities have made many attempts to develop natural alternatives to the traditional fossil-based diamines. In fact, some renewable diamines, *i.e.*, Priamine™, have already reached the market level, while others are expected to reach it in the near future.^{142,143} For instance, Cathay Biotechnology¹⁴² has recently scaled up the biosynthesis of cadaverine from natural sources, while the bio-process for the production of 1,4-diaminobutane is expected to be developed on the industrial scale in the next few years. This reflects the increasing interest in the utilization of bio-based diamines. Their industrial production is expected to reach a very high market demand in the near future given that they will be employed not only in the synthesis of NIPU but also in the production of bio-based polyamides.¹⁴³

3. Synthesis of NIPU foams

In this section, we provide a general overview on the preparation of NIPU foams. As mentioned in the Introduction, it has been reviewed that aminolysis between CCs and diamines represents the most investigated polymerization route to obtain NIPUs in general and NIPU foams.^{13,31,32,39,48} The presence of CCs allows several OH pendant groups to be achieved in the resulting polyhydroxyurethane chain, which are crucial in the reprocessability of the material (see Section 5).

The selection of different CC and diamine structures and functionality, as well as the ratio of CC/NH₂ groups determine

the different degrees of crosslinking, and thus the mechanical, thermal, chemical/physical, and functional properties of the foamed materials. To prepare porous materials, either physical or chemical blowing agents are needed. However, the aminolysis process is slower than the conventional PU-based synthesis route, and thus quite short reaction times are needed to ensure gas trapping within polyurethane matrices and get porous structures.³⁴ Therefore, currently, this is the main limitation in the technology shift. In this sense, NIPU foam-blowing routes can be classified into two macro-categories, non-self and self-blowing routes, as will be discussed in the next sections.

3.1. Non self-blowing routes

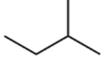
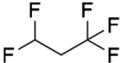
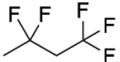
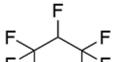
Non-self-blowing processes require the use of physical or chemical BAs to allow the formation of gases and let the blowing process progress.¹³ In the case of physical BAs, to accurately select physical BAs, it is crucial to verify their physical and chemical characteristics, such as boiling point and heat of vaporization from the viewpoint of economy and process safety.² In detail, lower boiling temperature BAs enable controllable foaming reactions, resulting in a lower energy input and avoiding critical degradation temperatures for foams. The thermal conductivity (λ) of the physical BAs in the gas phase is crucial given that it plays a significant role in determining the final conductivity of the resulting NIPU foams. Another relevant aspect is the Global Warming Potential (GWP) factor, an estimation of the ozone depletion according to the Montreal and Kyoto Protocols.^{2,145} The physical BAs used in synthesis of non-self-blowing NIPU foams are summarized in Table 3.

Preliminary investigations on NIPU foams focused on the use of low-boiling physical BAs. Figovsky and co-authors patented in 2004¹⁴⁶ the synthesis of acrylic NIPU foams through the radical polymerization of acrylate, whereas the blowing reaction could be carried out by using low-boiling HCs such as pentane or cyclopentane.^{146–149} Subsequently, non-isocyanate sprayable materials were also patented by the same research group in 2015.¹⁵⁰ Specifically, two different mixtures called amino-reactive components, *i.e.* a mixture of epoxy and cyclocarbonate functional groups, and amino-containing groups, *i.e.* primary amine, were properly mixed in a reaction chamber and the resulting system was conveyed through an intermediate chamber, where the process parameters can be controlled, and then sprayed onto a clean surface through a nozzle. For the blowing reaction, the authors proposed several physical BAs such as HCs or both saturated and unsaturated HFCs, *i.e.*, HFC-365mfc or HFC-234fa. As a result, the sprayed foams, *i.e.*, with open/closed cell characteristics, were found to be tack-free within 60 s, with a thermal transmission exceeding $0.5 \text{ W m}^{-2} \text{ K}^{-1}$.

The use of sustainable precursors in the synthesis of NIPU foams was proposed by Blattmann *et al.*,⁵⁰ where bio-based open cell NIPU foams with tailored properties were synthesized at room temperature. A suitable blend of rigid carbonated trimethylolpropane glycidyl ether polyglycidyl-ethers



Table 3 Physical properties and global warming potential (GWP) of physical BAs used to formulate non-self-blowing non-isocyanate polyurethane foams

Type of BA	Structure	Boiling temperature (°C)	Heat of vaporization (kJ mol ⁻¹)	Molar mass (g mol ⁻¹)	λ (mW mK ⁻¹) at 25 °C	GWP (-)	Ref.	
HCs	Pentane		36.1	27.6	72.1	16.4	11	Figvosky <i>et al.</i> ^{146–150}
	Cyclo pentane		49.1	28.7	70.1	18.76	11	Figvosky <i>et al.</i> ^{149,150} Marrucho <i>et al.</i> ¹⁵¹
	Iso-pentane		28.2	24.7	72.15	11.2	11	Figvosky <i>et al.</i> , ^{149,150} Peyrton & Avérous ²
HFCs	HFC-2345fa		15.3	26.0	134.1	12.5	990	Figvosky <i>et al.</i> , ¹⁴⁷ Peyrton & Avérous ²
	HFC-365mfc		40.2	26.0	148.1	11.6	910	Figvosky <i>et al.</i> ^{148–150}
	Solkane 365/277		30	—	149.6	10.1	725	Lauth <i>et al.</i> , ¹⁵² Blattman <i>et al.</i> ⁵⁰
	Supercritical CO ₂	O=C=O	-78.6	6.8	44	—	1	Grignard <i>et al.</i> ¹⁰³

HFC-2345fa is the commercial name of 1,1,1,3,3-pentafluoropropane, HFC-365mfc is the commercial name of 1,1,1,3,3-pentafluorobutane and Solkane 365/277 is the commercial name of the mixture of 1,1,1,3,3-pentafluorobutane (93 wt%) and 1,1,1,2,2,3,3,3-heptafluoropropane (7 wt%).

(TMPGE, 60 wt%) and flexible ethoxylated TMP (EO-TMPGC, 40 wt%) was employed given that they possessed both rigid and flexible features, providing adequate pot life and gelation times. HMDA and commercial ozone-free-HFC Solkane 365/277 were selected as the curing agent and BA, whereas DABCO 33 was selected as the gelling catalyst (1 wt%). This route represents an easy one-pot process to obtain flexible NIPU foams within a relatively short time (20–30 min) at room temperature. As a result, foams with open cells ranging from 132 μm to 184 μm and apparent density in the range 83–219 kg m^{-3} , were obtained. The smallest pores and density as well as the highest height were achieved at the shortest mixing time, corresponding to a lower viscosity of the reaction mixture.

Based on this technology, a patent was released by the French company Faurecia Interieur Industrie for the production of NIPU foams for the automotive sector.¹⁵² However, the resulting foams possess a high apparent density, corresponding to poor foaming conditions, which limits their use. Conclusively, non-self-blowing routes have produced flexible and semiflexible NIPU foamed materials with an apparent density of 400 kg m^{-3} in most cases, making them applicable in the automotive sector as integral foams, *i.e.* for car seats and steering wheels. However, some environmental and toxicity issues should be noted such as the use of physical BA with high GWP and relatively high boiling temperatures, which can lead to high foaming temperatures, and thus compromise their stability.

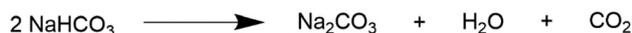
Closed cell structures with a low density (30–100 kg m^{-3} , rigid foams) and rather low thermal conductivity ($\lambda = 50$ mW

$\text{m}^{-1} \text{K}^{-1}$) were for the first time prepared using supercritical CO₂ (sc-CO₂) as a BA at high temperature and high pressure.¹⁰³ In particular, sc-CO₂ has been widely recognized as an inert and green physical blowing agent, enabling the fine-tuning of rigid microcellular structures.^{153–155} Foams were synthesized using a single-step procedure employing a bio-based amino-telechelic oligoamide and cyclic carbonates obtained from epoxidation of soybean oil at 80 °C for 3 h, and by impregnating sc-CO₂ within polymer matrices at different times and pressures. The blowing reaction was carried out by pressurizing CO₂ at a temperature close to the melting point of the polymer matrix, while expansion took place due to rapid decompression.¹⁰³ It was demonstrated that long impregnation times promoted higher CO₂ solubility within the polymeric matrix, and thus the formation of narrow and small closed cell morphologies (in the range of 4–22 μm), which was ascribed to high melting temperature (T_m) of the polymer matrix, corresponding to enhanced cell nucleation and the melt strength during foaming. Alternatively, higher pressure (300 bar) induced a more homogenous cell size distribution (range 2–5 μm), translating to low thermal conductivity, which was found comparable to that of conventional thermal insulating materials such as glass wool and wood.¹⁵⁶ Recently, Mao *et al.*¹⁵⁷ suggested an sc-CO₂-assisted-foaming process by employing a bisphenol A diglycidyl ether (EOBPA)-based cyclic carbonate oligomer and bio-based diamine (HMDA). sc-CO₂ was utilized under lower pressure conditions than in ref. 103 (150 bar) and 80 °C for 6 h. The partially bio-based NIPU



foams exhibited rigid structures with an average size of 9–22 μm , corresponding to the maximum compressive strength between 120–150 kPa and accomplishing overall compressive behavior close to that of conventional PU foams. Although the use of green physical BA is promising, it should be noted that the use of supercritical CO_2 requires specific pressurized conditions, and thus high-cost devices, which may limit the scaling-up of this process.

Besides the use of physical BAs, another valid approach involves exploiting the thermal decomposition of inorganic salts, such as sodium bicarbonate (NaHCO_3), to generate CO_2



Scheme 7 Blowing route based on the decarboxylation of inorganic salts (i.e., sodium bicarbonate).

and water (Scheme 7). This is a green and human-safe approach as well as a widely consolidated route to synthesize foams from thermoplastic materials.³ Usually, this decomposition occurs at around 145 $^\circ\text{C}$ –150 $^\circ\text{C}$, which matches the chemistry of NIPU foams, as reported by the recent patent by Zeller and Carter¹⁵⁸ and the study by Amezúa-Arranz *et al.*¹⁵⁹ In the latter work, the authors studied the effect of the particle size distribution and concentration of NaHCO_3 , given that both have an impact on the foam reactivity. The best results were obtained using 13 mm particles, attaining a good compromise between the polymerization and blowing reactions, whereas the narrowest pore size distribution was achieved using the highest SC concentration (1.5%), corresponding to relatively low-density foamed systems.

Table 4 summarized the most significant non-self-blowing routes together with their potential environmental impacts and applications.

Table 4 Literature review of non-self-blowing non-isocyanate polyurethane foams

Cyclic carbonates	Diamines	Physical BAs	Reaction <i>T</i> and time	Foam morphology	Properties	Applications	Environmental/toxicity/process drawbacks aspects	Ref.
CCs	Primary diamines	HFC, pentane, cyclopentane	80 $^\circ\text{C}$, 3 h, 80 $^\circ\text{C}$, 4 h, 120 $^\circ\text{C}$, 2 h	Open cells	ρ in the range of 200–600 kg m^{-3} , tear strength in the range of 3–3.5 MPa, elongation strain >50%	Seating	Use of high GWP-BAs, not sustainable building blocks for precursors are not included. Relatively high-boiling temperature-BAs	Figvosky <i>et al.</i> ^{149,150}
TMPGC/EO-TMPGC	HMDA	Solkane 365/227	80 $^\circ\text{C}$ for 2–6 min, curing at 80 $^\circ\text{C}$ for 14 h	Open cells	$\rho = 80$ –220 kg m^{-3} , cell size = 130–180 μm , hysteresis = 13%, hardness = 3 kPa	Automotive	Low VOC emission, formaldehyde-BA, poor foaming (high-density)	Blattman <i>et al.</i> , ⁵⁰ Lauth <i>et al.</i> ¹⁵²
PEG-bisCC, Soybean oil CCs	1,2-Diaminoethane	Sc- CO_2	120 $^\circ\text{C}$ for 3 h or 24 h	Closed cells	$\rho = 110$ –180 kg m^{-3} $\lambda = 50$ –60 mW mK^{-1}	Thermal insulation	Ecofriendly process/Solvent free High cost of supercritical CO_2 equipment High pressure and timing reaction. Higher λ and high density compared to that of conventional PUs	Grignard <i>et al.</i> ¹⁰³
ECBPA-based CC	C36 Alkylendiamine HDMA EDA	Sc- CO_2	80 $^\circ\text{C}$ for 6 h, at 150 bar	Closed cells	ρ in the range of 32 and 215 kg m^{-3} with pore sizes of 10–20 μm , compressive strength in the range of 49.5 and 123.4 kPa	Not indicated	Ecofriendly process/solvent free High cost of supercritical CO_2 equipment, high-density foams (poor foaming)	Mao <i>et al.</i> ¹⁵⁷
Tris-CCs	HMDA	NaHCO_3	150 $^\circ\text{C}$ for 6 min	Open cells	$\rho = 220$ –500 kg m^{-3} Cell size ranging from 150 to 390 μm	Not indicated	Ecofriendly process, high temperatures required	Amezúa-Arranz <i>et al.</i> ¹⁵⁹



3.2. Self-blowing processes

Self-blowing, also named self-foaming, involves *in situ* gas formation with the aid of chemical reactions. According to the definition given in the review by Detrembleur and co-authors,¹⁶⁰ self-blowing routes involve the incorporation of chemical blowing agents covalently bound to a polymeric matrix, promoting its expansion by the production of gaseous compounds. Based on their mechanism, self-blowing routes are classified into thermolysis and condensation-based routes¹⁶⁰ (Fig. 3).

In the first case, blowing is induced by the thermal degradation of chemical BAs anchored to the polymeric matrix, leading to the formation of volatile compounds, such as CO₂, water, and alcohol. Condensation routes are endogenous systems, where blowing takes place simultaneously with curing, involving condensation reactions between the functional groups of the precursors and producing expanded materials. Usually, small molecules are employed such as water, thiols, and alcohols. In the synthesis of NIPU foams, two approaches have been selected. In the case of thermolysis, foam formation is driven by the thermal decarboxylation of carbamates, either directly or facilitated by the presence of carbonates or carboxylic acids. Condensation routes involve the reaction of siloxane-based BAs with diamines and the reaction of cyclic carbonates with either thiols or water, *i.e.* S-alkylation and hydrolysis, respectively.

The most significant chemical BAs employed in self-blowing routes are illustrated in Fig. 4.

In the following sections, the foaming routes are described together with the foam properties. The examined NIPU foams

are grouped based on their morphological characteristics, *i.e.*, open-cell and closed-cell structures, and the most relevant morphological, thermal, chemical, physical, and mechanical properties are reviewed.

3.2.1 Foaming based on siloxane/amine condensation. The blowing route based on the reaction with diamines was proposed for the first time in 2015 by Cornille *et al.* for the synthesis of flexible/semiflexible foams.⁴⁹ The authors proposed aminolysis between petrol-based 5CCs and diamines, followed by a blowing reaction assisted by poly-methyl-hydroxysiloxane (PMHS, commercial name, Momentive MH15, Fig. 4 and Scheme 8). The SiH groups in PMHS reacted with diamines, yielding silazane groups and hydrogen (H₂), which promoted the expansion.⁸ Because of the extremely slow reaction rates and low yields, suitable polymerization catalysts, such as thiourea and TBD,⁴⁹ were crucial to accelerate the polymerization reaction. Overall, the aminolysis was conducted at 80 °C for 12 h, followed by curing at 120 °C for 4 h.

The effect of the two types of petrol-based cyclic carbonates, *i.e.* poly(propylene oxide) bis-carbonate and trimethylolpropane tris-carbonate (TMP-Tri-C5) and conventional diamines (Jeffamine EDR 148 and Priamine 1073), on the final characteristics of flexible foams was examined. Five different formulations were obtained depending on the functionalities of the selected cyclic carbonates as well as their chemical structures. Therefore, foamed materials with various morphological characteristics, ranging from semi-flexible to flexible materials, with coarse and interconnected pores

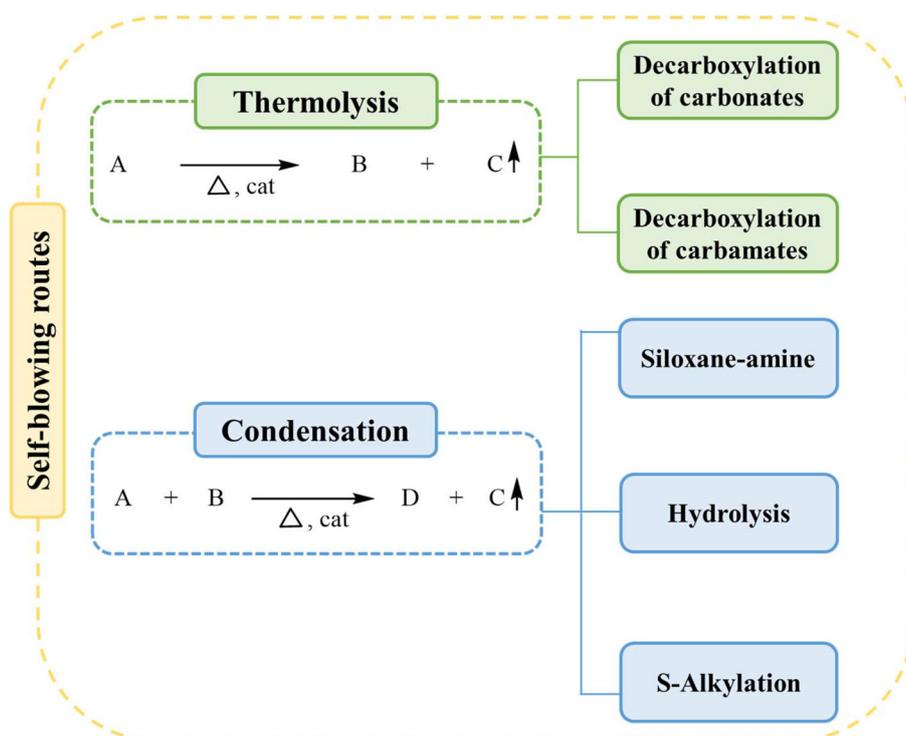


Fig. 3 Schematic of the self-blowing reactions employed in the synthesis of NIPU foams.



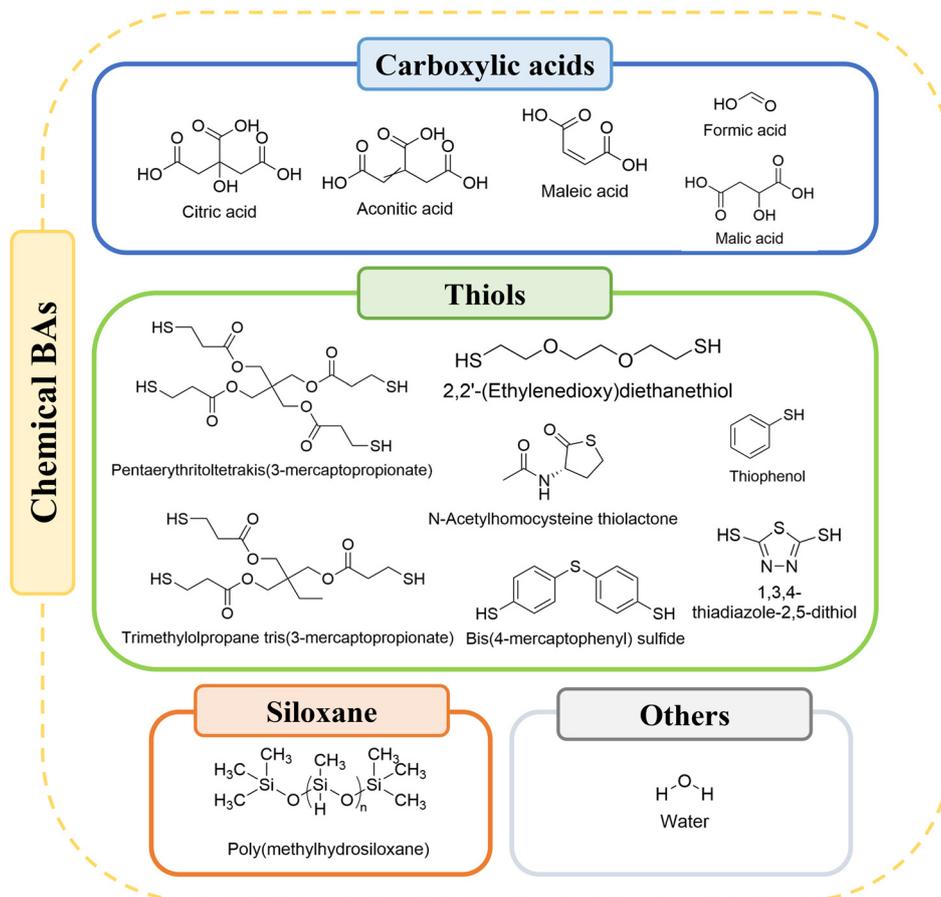
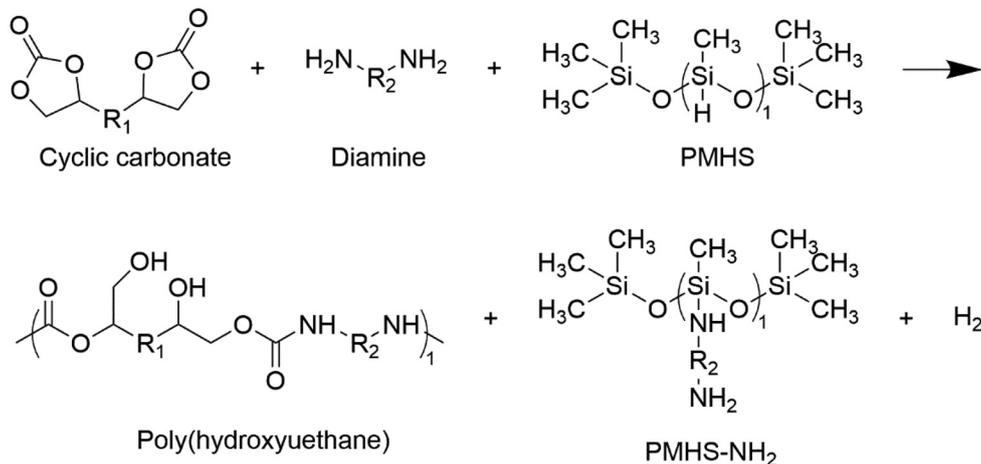


Fig. 4 Chemical BAs used in the synthesis of self-blowing NIPU foams.



Scheme 8 Blowing reaction between PHMS (MH 15) and diamine. Reproduced from ref. 49 with permission from Elsevier Ltd., Copyright (2015). License Number 6034151206250.

(1000–1500 μm -average size), as well as different apparent densities (190–300 kg m^{-3}), were produced (Fig. 5).

The proposed route to formulate NIPU foams required long reaction times and high-temperature conditions, followed by

similar curing times, making it practically unfeasible for upscaling purposes; the aminolysis route at room temperature was implemented by the same authors in a later publication,¹⁶¹ although with extremely long reaction times of



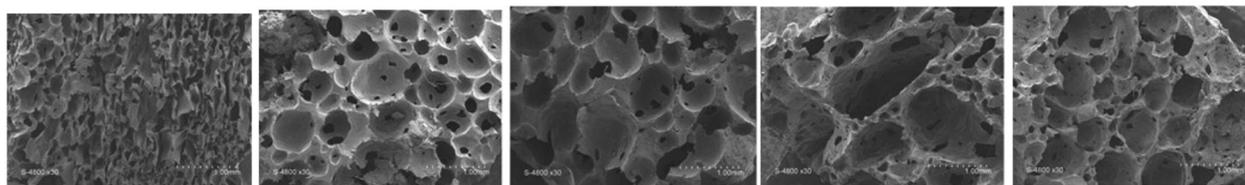


Fig. 5 SEM images of developed NIPU foams using PHMS as the blowing agent. Reproduced from ref. 49 with permission from Elsevier Ltd. Copyright (2015). License Number 6034151206250.

about three days. Another relevant work was published by Coste *et al.*,¹¹⁰ where tetrafunctional 6CC from petrol-based sources was selected as precursors, together with diamines with different reactivities (IPDA, cadaverine, Priamine®, and MXDA). This selection enabled the aminolysis process to be carried out at lower operating temperatures (50 °C for 4 h) in the absence of catalysts. As a result, the chemical structures of the diamines implied that different gel times corresponded to different chemical and physical characteristics of the foams. Specifically, diamines with higher reactivity and no steric hindrance allowed gel times (200–400 s) closer to that of conventional PU foams to be achieved. Nonetheless, also in this case, the use of petrol-based precursors was still implicated.

Sustainable rigid NIPU foams based on lignin-derived-cyclic carbonates, obtained through the above-mentioned blowing route, were synthesized *via* a blowing reaction between diamines and PHMS for the first time by Sternberg & Pilla in 2020.^{99,162} As mentioned in Section 2.1.1, this work is at the vanguard in the preparation of sustainable NIPU foams from industrial Kraft lignin, overcoming its limitations by proposing a green route that enabled to develop both cyclic carbonate precursors and curing agents. In this case, blowing was carried out using PMHS at 1.5% and 3.0% volume fraction of the total reaction mixture, followed by curing at 150 °C for 4 h. As a result, the rigid foamed materials showed comparable gelation times in the range of 3 min with respect to the conventional PU foams, owing to the combination of high aromaticity provided by the lignin-based precursors and the elasticity of the aliphatic fatty acids-diamines. The obtained rigid foams exhibited porosities in the range of 0.7–0.8% and compressive strengths exceeding 100 kPa under the investigated conditions.

Using a similar foaming route, Li *et al.*¹⁶³ suggested the synthesis of lignin-based NIPU foams for wound dressing applications. The addition of silver nanoparticles at different concentrations in the polymeric matrix allowed remarkable antimicrobial properties to be achieved against common pathogens such as *Staphylococcus aureus* and *Escherichia coli* (up to 95%).

Conclusively, the use of PHMS as a chemical BA may be associated with potential flammability issues owing to the release of H₂. Moreover, the employed operating conditions are still not comparable with that of conventional PU foams as well as the use of precursors from non-sustainable sources, making this foaming route not completely captivating from an

environmental point of view. Concerning the foam properties, both open and closed-cell structures presented high apparent densities in the range of 200–400 kg m⁻³ with performances lower than that of their PU counterparts (Table 5). Additionally, it can be concluded that mainly open-cell foams have been synthesized through this foaming route, which limits their applicability.

3.2.2 Foaming based on decarboxylation of carbonates

3.2.2.1 Thermally and carboxylic acid-driven decarboxylation.

Decarboxylation of bis-cyclic carbonates was introduced in 2018 by North and co-workers¹⁰¹ (Scheme 9). The process involved the formation of bis-carbonates, which can react with diamines, to get PHUs *via* a solvent-free polymerization, whereas no chemical BAs are needed and *in situ* CO₂ is generated. The examined work represents an important contribution to NIPU research, given that foamed materials with high renewable content (≥90%) were obtained utilizing bio-based building blocks, *i.e.*, sorbitol and L-lysine for the synthesis of CCs and diamines (*e.g.*, cadaverine), through a solvent-free and thermally driven-process. The synthesis was carried out at 100 °C to get rigid-foamed materials, whereas CO₂ is well entrapped in the polymeric matrix. A similar approach was selected by Anitha *et al.*¹⁰⁰ to prepare flexible NIPU foams at room temperature for 18 h by selecting resorcinol diglycidylether-based cyclic carbonates and amine-terminated oligomer phenylhydroxylamine (AOPHA), whereas the process was catalyzed by TBD. However, this special route requires harsh conditions and unique chemical compounds (*i.e.*, sorbitol-based), which makes it rather unpractical in many cases.

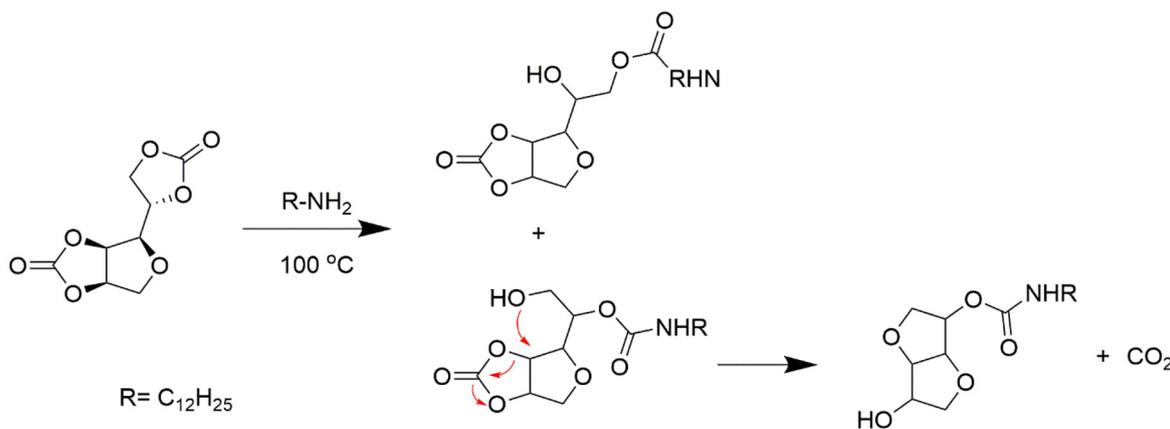
Other decarboxylation routes have been reported, whereas acid chemical BAs, *i.e.*, citric,^{57,117,118,164,165} aconitic, malic, and maleic¹⁶⁶ and formic acids⁵⁷ (Fig. 3), have been involved. Glutaraldehyde is indicated as a curing agent, which easily reacts with amine groups.

In the publications by the group of Pizzi,^{57,117,118,164} bio-based dimethyl carbonates from mimosa tannin were synthesized and reacted with diamines to get an NIPU resin (defined as tannin-based non-isocyanate polyurethane foams, TNIPU). Interestingly, closed/open-cell systems were obtained with relevant specific compressive strength (higher than 1 kPa kg⁻¹ m⁻³). Moreover, the flame retardant properties were tested, resulting in comparable features of the conventional PU foams with a limiting oxygen index (LOI) of 27.5%.¹⁶⁴



Table 5 Review of NIPU foams obtained through blowing reaction using PHMS

Cyclic carbonates	Diamines	Process conditions	Morphology	Properties	Applications	Ref.
PPO-Bis-C ₅ /TMP-Tri-C ₅	Priamine 1073/ Jeffamine® EDR-148	80 °C, 24 h, curing at 80 °C for 14 h or 25 °C for 3 days	Open cells	ρ in the range of 100–200 kg m ⁻³ Thermal stability >300 °C	Integral foams for automotive (seating, steering wheel)	Cornille <i>et al.</i> ^{49,161}
Lignin-based CC	Priamine 1074	80 °C for 4 h, 150 °C for 4 h, 80 °C for 2 h, curing at 150 °C for 12 h	Open/closed cells	ρ in the range of 100–300 kg m ⁻³ $E = 1.1$ – 1.7 MPa, σ (10%) = 105–180 kPa, hysteresis loss = 19–37%	Insulation, packaging	Sternberg & Pilla ^{99,162}
Lignin-based CC	Petrol-based diamine (@China Evolution Technology Co)	1 : 2 CC/NH ₂ , silver nanoparticles at 6.5%, 8% and 10%, curing at 150 °C for 12 h	Open cells	Compressive strength at 50% in the range of 28–200 kPa Thermal stability > 350 °C, 99% cell reduction for <i>S. aureus</i> and <i>E. coli</i> within 8 h	Wound dressing	Li <i>et al.</i> ¹⁶³
6-Membered CC (TC6)	MDXA, triethylamine, isophoronediamine, cadaverine	50 °C, overnight. Curing at 120 °C for 2 h	Open/closed cells	ρ in the range of 150–300 kg m ⁻³ , cell size = 210–1000 μ m, σ (50%) = 140–250 kPa	Insulation, packaging	Coste <i>et al.</i> ¹¹⁰

**Scheme 9** Thermally driven decarboxylation of bis-cyclic carbonates derived from sorbitol. Reproduced from ref. 100 with permission from Elsevier Ltd., Copyright (2022). License Number 6034160465054.

However, it must be emphasized that the use of glutaraldehyde implies environmental and health issues.³²

Table 6 summarizes the foaming routes based on decarboxylation and the respective NIPU foams together with their properties and potential applications.

3.2.2.2 S-Alkylation. S-Alkylation (or thiolization, Scheme 10a) offers a greener alternative condensation route to produce hybrid NIPU foams, known as NIPTU, utilizing thiols (–SH) as blowing agents.

The thiol compounds mentioned in the literature are shown in Fig. 3. To date, mainly aliphatic ester- and ether-based compounds have been employed as blowing agents, *i.e.*, 2,2'-(ethylenedioxy)diethanethiol. However, aromatic-based thiols have recently gained attention. They are alternatives to aliphatic thiols owing to their higher basicity, corresponding to higher reactivity and lower gelling times. The group of

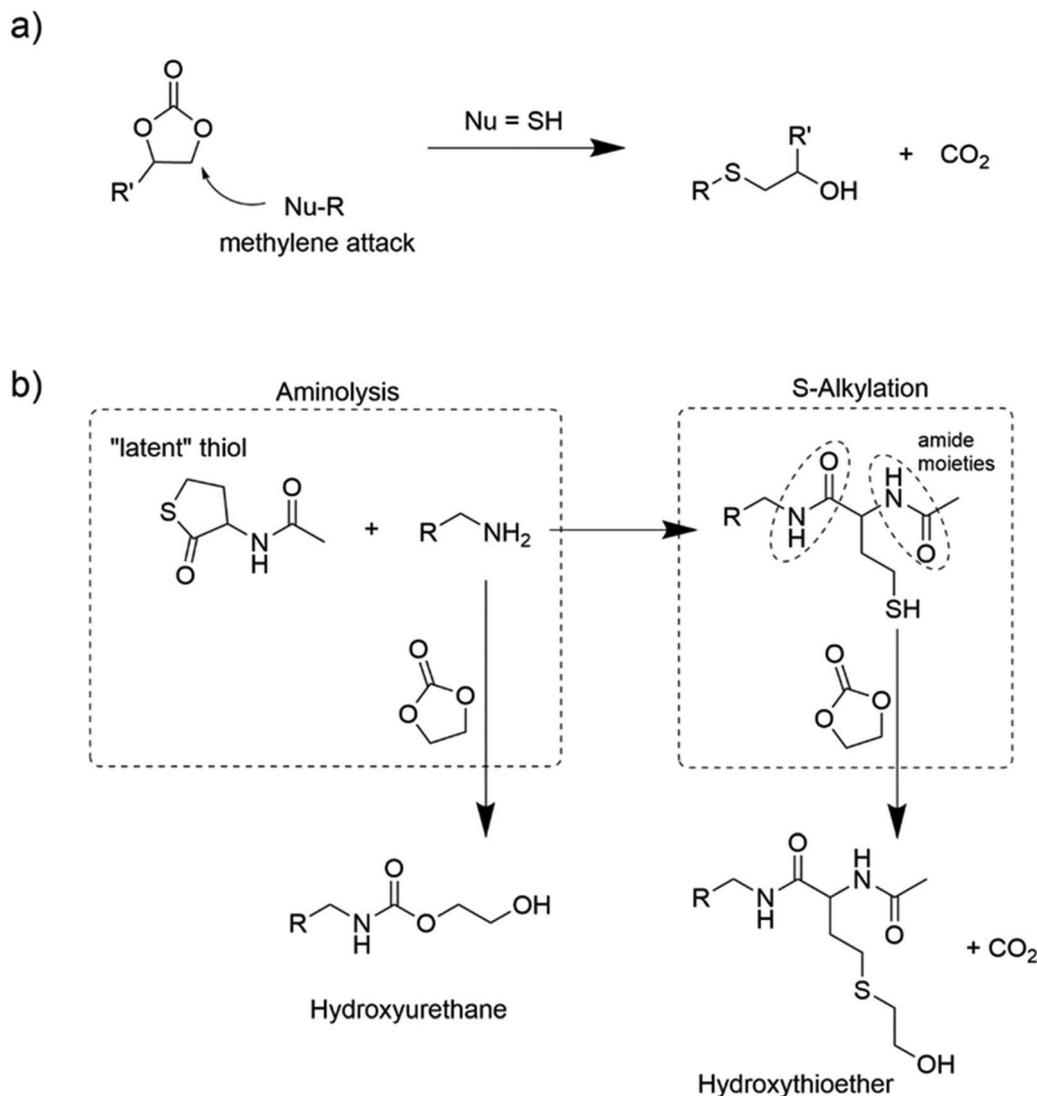
Detrembleur introduced S-alkylation in 2020¹⁶⁷ through the nucleophilic addition of a thiol-(ether (ethylenedioxy)diethanethiol) to diacyl-carbonates (Pearson's reaction) to obtain hydroxy thioether and CO₂ (Scheme 10a).

The authors investigated the regioselectivity of the aminolysis/S-alkylation, examining different organo-based catalysts, such as DBU, TBD, DABCO. It was found that, although aminolysis can be carried out without the use of a catalyst at 80 °C, S-alkylation requires suitable organo-based catalysts. Specifically, in the presence of DBU, the resulting foamed materials presented high-density-flexible-like structures (200–400 kg m⁻³), whereas the dimensional stability was achieved owing to the combination of adequate polymerization and expansion. Specifically, strategies were adopted to enhance foaming and reduce the bubble coalescence, such as higher operation temperature (up to 120 °C), pre-polymeriz-



Table 6 Review of NIPU foams obtained through decarboxylation

Carbonate-based precursors	Diamines	Decarboxylation agents	Process conditions	Morphology	Properties	Applications	Ref.
Bis-carbonate-sorbitol derived-CC	HMDA Cadaverine	Temperature	100 °C for 20 h	Closed cell	Thermal stability >250 °C T_g about 6 °C	Not indicated	Clark <i>et al.</i> ¹⁰¹
Dimethyl carbonate from mimosa tannin	HMDA	NaHCO ₃ /maleic acid	25 °C for 5 h and curing at 103 °C for 4 h	Closed cell	Thermal stability > 300 °C	Not indicated	Xi <i>et al.</i> ^{117,118}
Dimethyl carbonate from tannin	HMDA	Formic acid	83 °C for 10 h	Closed cell	Maximum compressive strength = 0.8 MPa, LOI = 24.45%	Fire proofing	Zhao <i>et al.</i> ⁵⁷

**Scheme 10** (a) S-Alkylation of CCs with thiols.¹⁶⁷ (B) S-Alkylation of CCs with latent thiols and aminolysis of CCs. Reproduced from ref. 52, with permission from the American Chemical Society, Copyright (2022).

ation under ambient conditions or by employing nucleating agents and surface stabilizers, by tailoring microcellular characteristics.¹⁶⁷

Subsequently, S-alkylation has been widely recognized as a valuable self-blowing route to prepare NIPTU foams with different characteristics,^{45,52,97,168} where sustainable precur-



sors, for instance, from the epoxidation of vegetable oils such as CNSL, linseed oil and dimeric acid were employed, achieving a sustainability index of $\geq 80\%$.⁸⁹ The process was carried out under high-temperature conditions between 80 °C–120 °C, although the alkylation process was optimized, resulting in shorter gelling times.

Purwanto *et al.*^{52,168} examined the effect of the thiol concentration and type on the final characteristics of the foamed materials. In the first work,⁵² employing the same reaction conditions and thiol compound, as reported by Monie *et al.*, investigated the *S*-alkylation route through a rheologically guided approach, whereas under the investigated conditions (120 °C), the gelling times were drastically reduced from several hours to 20 min. A structure–property relationship was proposed for the first time according to the well-established Gibson–Ashby model,^{2,11,45,169} correlating the mechanical performances with the cellular struts and the apparent density. Tunable characteristics (rise height, foam density, and cellular parameters) were achieved by varying the thiol concentration.

In a subsequent work,¹⁶⁸ the authors focused their attention on the use of aliphatic thiols with different functionalities (from 2 to 4, S2, S3, and S4) reacting with bio-based CC obtained from the epoxidation of a dimeric acid called GS-120 to modulate the final characteristics of the foamed materials. In all these cases, open-cell foams were obtained (Fig. 6a), with a nice narrow size distribution in the range of 0.2–0.3 mm. The effect of the chemical structure of the thiol was crucial to obtain different cross-link structures, resulting in different compressive properties; at increased thiol functionalities, the compressive and cyclic compressive properties increased, being three or four times higher than that of functionality equal to 2 (Fig. 6b).¹⁶⁸

However, it is noteworthy that the use of thiols may be associated with the release of volatile organic compounds (VOCs) or some leaching and toxicity issues, and therefore as already described in Section 2.2.2, an interesting way to overcome these issues is to “mask” thiols. This process involves incorporating them into a polymeric matrix, by either employ-

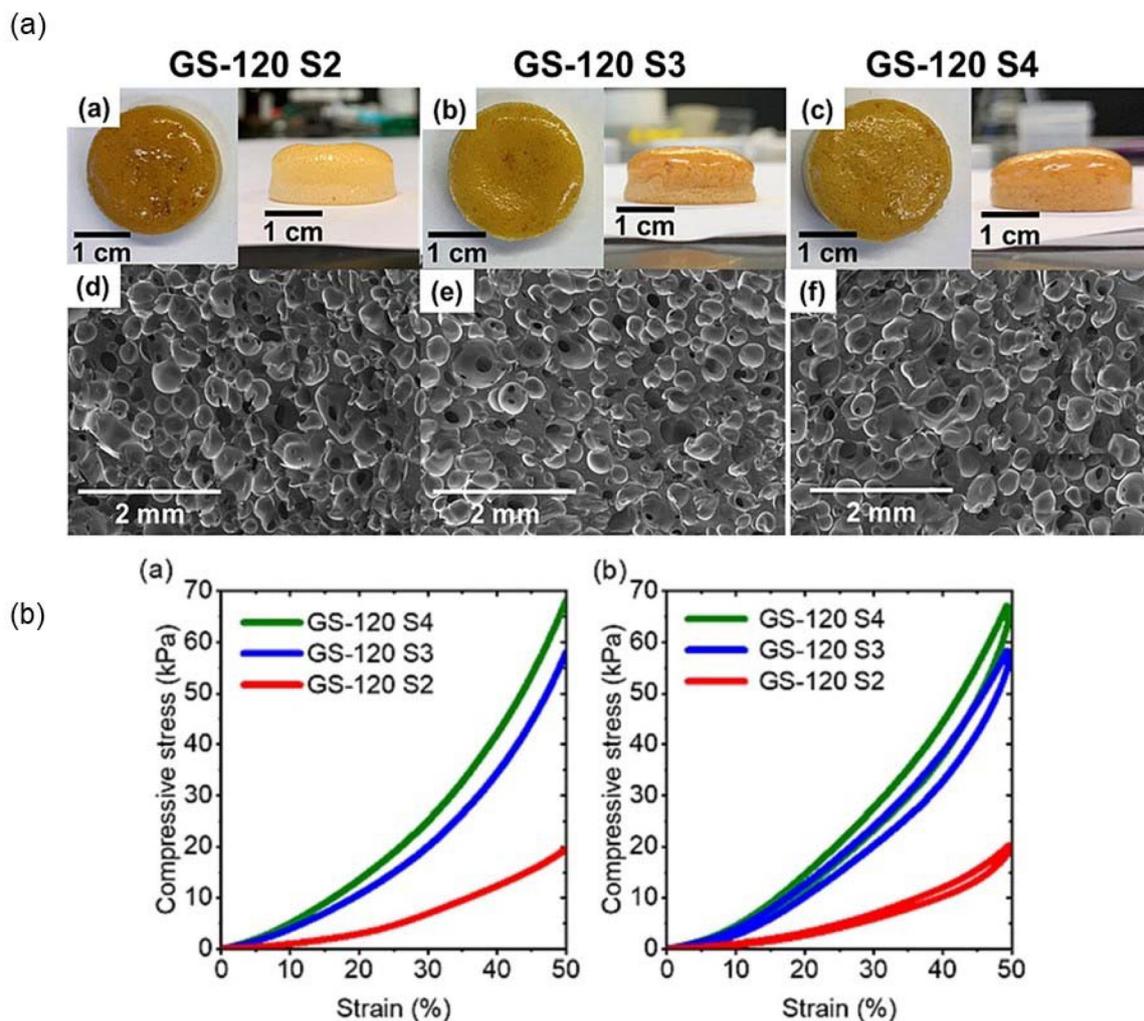


Fig. 6 (a) Digital and SEM images of NIPTU foams with different thiols. (b) Compressive and cyclic compressive stress vs strain curves of the selected foams. Reproduced from ref. 168, with the permission from Elsevier Ltd, Copyright (2024). License number 6034161388565.



cycling and reprocessability of the foam *via* compression molding and re-utilizing it as polymeric films (see Section 4).

Regarding the chemistry of the process, the authors prepared different materials starting from conventional tris(cyclic carbonate) and by screening different amines (both aromatic and aliphatic) as well as temperature and reaction times (80 °C and 100 °C at 3 h and 5 h) and water contents.

Under the selected conditions, it was found that aminolysis yield exceeded 90% within 30 min. Foams with flexible and rigid morphologies were obtained, whereas the addition of nanoclays, *e.g.* hydrotalcite at 12 wt%, was also fundamental for homogenizing the resulting cellular structures (Fig. 7a). Overall, self-blown foams showed thermal and mechanical behaviors, approaching that of PU materials including compressive strength of 40% in the range of 0.1–0.20 MPa (Fig. 7b, top images). The implementation of the selected technology on a larger scale was demonstrated for the first time; in particular, reaction injection molding (RIM) was selected to fabricate NIPU foams in a closed preheated mold of defined shapes (Fig. 7b, bottom images). A solvent-free route was proposed through pre-heating at 100 °C and subsequent injection of the precursor mixtures into the preheated mold. The final NIPU foam characteristics were found to be comparable with that of the foams obtained at a lower scale. This represents the first real approach to scale-up this route on a real case, *i.e.* RIM technology.⁵¹

However, it should be noted that this approach, although promising, is only suitable for established PU technologies, requiring high temperatures, such as RIM. Therefore, in this case, epoxy-based click reactions were also suggested by the same authors to prepare NIPU foams under ambient conditions⁵³ through cascade exothermic reactions, as follows: (1) aminolysis of CC, (2) hydrolysis of CC and (3) aminolysis of the epoxy monomer. More specifically, the authors demonstrated that partial replacement of TMPC with the equivalent epoxy monomer (TMPE) resulted in rapid foaming (in 3 min), having high foaming reactivity. Several hybrid foams with open/closed cell structures with a density less than 500 kg m⁻³ having different thermomechanical properties according to the employed epoxy concentrations were obtained; at lower concentrations, T_g was about 21 °C, similar to other NIPU foams, while, at higher concentrations, T_g was about 35–40 °C, closer to that of epoxy monomers. Interestingly, the foams were also synthesized by selecting bio-based precursors such as glycerol-based CC and epoxy (GTC and GTE) and bio-based diamines (HMDA) and natural fillers, whose properties were found to be comparable to that of conventional PU foams (apparent density lower than 300 kg m⁻³ and GC higher than 90%), achieving high levels of sustainability (90%). Conclusively, the combination of CC hydrolysis with a click reaction presents the most promising approach for synthesiz-

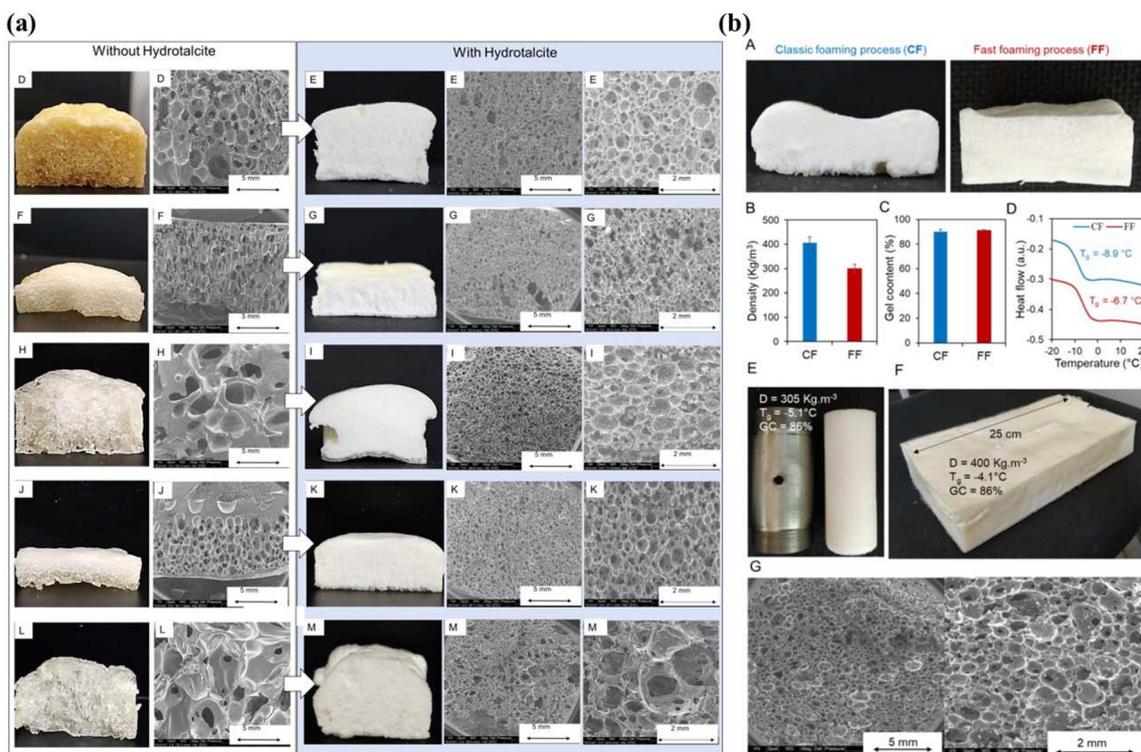


Fig. 7 (a) Morphological investigation of the obtained foams with and without reinforcing filler (hydrotalcite). (b) Comparison between classic foaming process (left) and fast foaming process (right): density, gel content, and thermal properties (top images). Upscaling of NIPU foam production up to 650 g in a closed mold, and SEM images of the scaled-up formulation (bottom images). Reproduced from ref. 51, with permission from John Wiley & Sons, Copyright (2022). License number 6034200603992.



resulting NIPU foams.^{51–53,167,168} However, in compliance with the 3R principle of the circular economy plan, reuse, reduce, recycle, presented by the European Commission in 2015,¹⁷⁴ a potential solution is to use natural or waste materials from agricultural or industrial sources as fillers. This is an established practice for conventional PU materials, whereas both organic and inorganic fillers have been widely used, such as lignocellulose,^{11,19,175,176} proteins from agricultural sources such as walnut shells, rice husk, potato, and chitin^{2,177–179} or animal waste from industrial production, *e.g.* eggshells, chicken feathers, and leather waste.^{180,181} It has been demonstrated that these fillers, once intercalated within PU matrices, enable remarkable mechanical and functional performances within specific concentration ranges, as well as reduce the environmental impact of the material. Therefore, the same concept can be easily extended to NIPU foams.

In this regard, a relevant contribution was recently reported by Trojanowska *et al.*⁵⁶ Different types of bio-fillers, such as keratin, cellulose, gelatin, zein, chitosan, and sodium lignosulfonate, were employed at different concentrations, ranging from 10 wt% to 30 wt%. More specifically, the authors focused their attention on the use of proteins with different amino acid compositions, *e.g.* cysteine, alanine, lysine, tryptophan, and prolamine, being sources of thiol groups. This allowed the *S*-alkylation of 5CCs to be performed without the aid of an external chemical BA (Fig. 8i). Surprisingly, operating at 100 °C for 5 h, the amount of thiol was not sufficient for *S*-alkylation; conversely, the evidence of foaming could be explained merely by the presence of the water content within the solid fillers, which was sufficient to promote the hydrolysis of 5CCs (Scheme 11). This represents a step forward in the production of self-blowing composite NIPU foams through the simple valorization of waste from the agricultural and industrial sectors, without the aid of further reagents. For a specific filler, the concentration effect is crucial to impart different characteristics to the foamed materials, *i.e.*, apparent density (between 200–400 kg m⁻³) and GC (80%–90%), whereas the lowest apparent density and the highest GC were found between 5 wt% and 20 wt%. Moreover, at a given concentration level (10 wt%), the effect of this type of filler was noticed in terms of morphological and mechanical properties (Fig. 8ii). After the proteins were selected, rigid and semi-rigid foams were obtained with compressive specific strengths (26.3 kPa kg⁻¹ m³), whereas the use of polysaccharides provided flexible foams with much weaker mechanical properties (0.7–6 kPa kg⁻¹ m³). The final properties of the foam were influenced by the dispersion of the type of fillers (*i.e.*, proteins or polysaccharides) within the PHU matrices, leading to distinct interactions and macromolecular rearrangements. This study opens the possibility to use biomass as a reinforcing/reactive component in PHU formulations, tuning the foam characteristics according to the filler selection. Further research is needed either to have full comprehension of the interaction between the bio-filler and the PHU matrices and explore the potential of different waste-derived fillers, for example, with different granulometric characteristics and using other natural

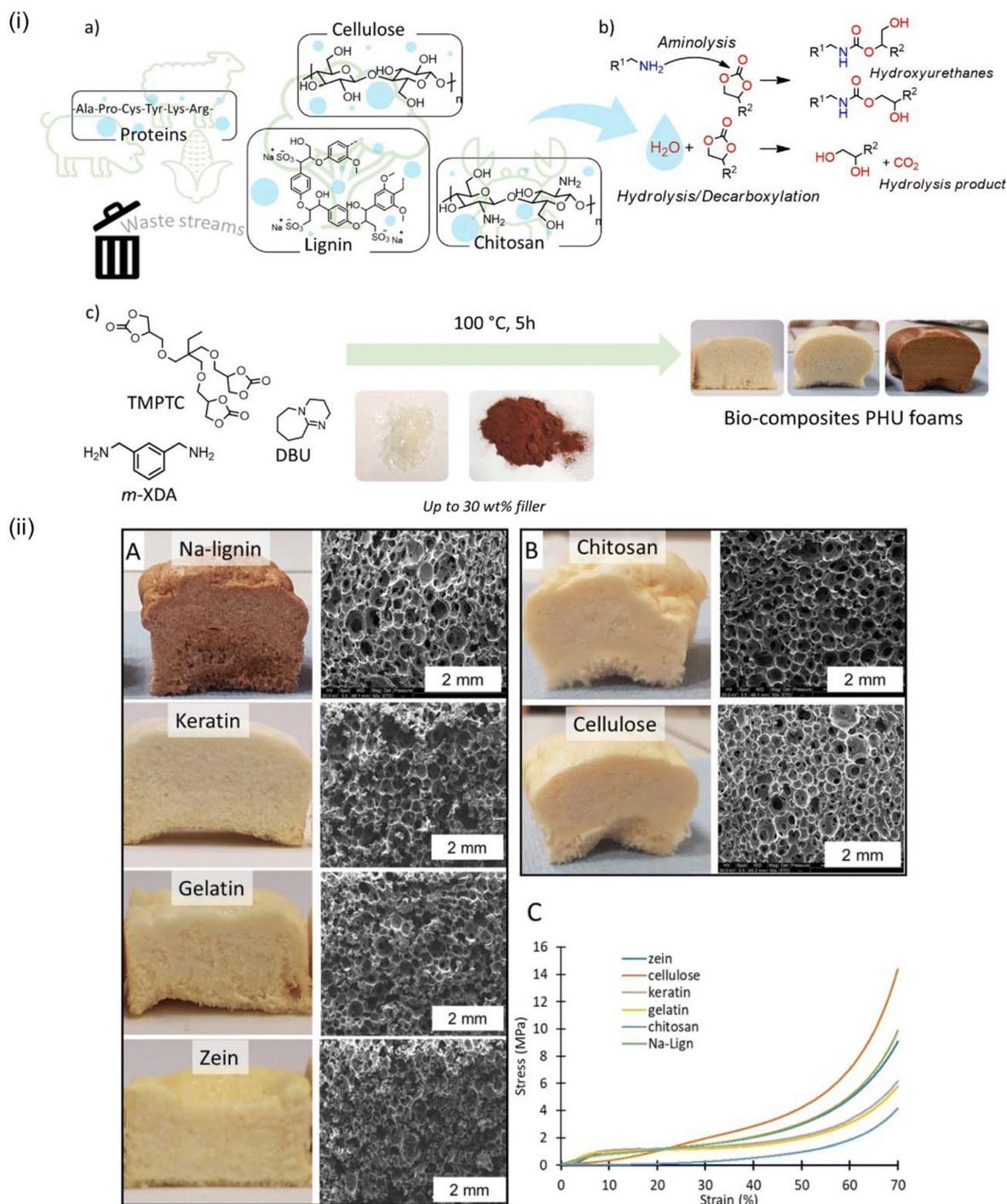
and waste sources, imparting specific functional characteristics, *i.e.*, thermal insulation. Attention should be shifted towards optimizing the synthesis route and preparing composite materials with comparable features to that of their composite PU counterparts.

5. Recycling and reprocessability of NIPU foams

The typical recycling of conventional PU foam systems primarily relies on mechanical methods, such as shredding, tearing, and grinding the foam and incorporating the resulting granules or powder as a filler in newly manufactured products. Chemical and enzymatic methods are also used, involving the depolymerization and cleavage of urethane bonds, followed by conversion into feedstocks such as polyol and isocyanate precursors.¹⁸² Subsequently, these feedstocks can be reintegrated to produce new-generation materials with advanced functional properties (*i.e.* upcycling), in line with the principles of the circular economy paradigm.¹⁸³ However, recycling pathways for isocyanate-free polyurethanes including foams have been poorly explored. The only reported evidence of chemical recycling of NIPU foams *via* hydrolysis was recently documented by Sternberg & Pilla.¹⁶² The authors investigated the recycling of lignin-based NIPU foam in an alkaline solution (0.1 M and 0.2 M KOH) and ethylene glycol (EG) under high pressure in an autoclave. Following the reaction, solid lignin was separated from the liquid mixture containing diamines and surfactant, which was then solubilized in dichloromethane (DCM). Upon precipitation of the mixture at pH 2, lignin powder was produced, which can be reused in the formulation of new-generation foamed materials. The authors compared the recycling yield of the hydrolysis process to that of the glycolysis route (using EG as a solvent) at various reaction times (2 h, 3 h, and 6 h). The highest lignin recovery of 93% was achieved with EG in 0.2 M KOH solution after 6 h. It was observed that the properties of the second-generation materials differed slightly from that of the virgin materials, with increased density and a lower compressive modulus.

In the case of conventional PU foams, which are thermoset materials, recycling and reprocessing are limited by their cross-linked structure. Consequently, the development of new recycling methods and reprocessing routes has become an important and rapidly growing field of research. To achieve this, dynamic covalent polymeric networks (DCPNs), also referred to as covalent adaptive networks (CANs),^{184–187} have been in development, and in recent years, have been proposed for the recycling of conventional PU foams¹⁸⁶ and PHU,^{187–189} NIPU,^{189–192} NIPU and NIPTU foams.^{45,167–169} CANs or DCPNs are stable under typical use conditions, but when exposed to specific external stimuli, such as temperature, UV light, pH, and solvents, their covalent bonds can rearrange. The incorporation of CANs allows the reprocessing of cross-linked materials, given that reversible bond breaking enables the material to flow upon heating. This significantly enhances





their reprocessability and recyclability, while also potentially providing properties such as shape memory and self-healing.

In particular, dynamic bonds and their associated reactions include ester, carbamate, urea, imine, disulfide, acetal, siloxane and silyl ester bonds, as well Diels–Alder

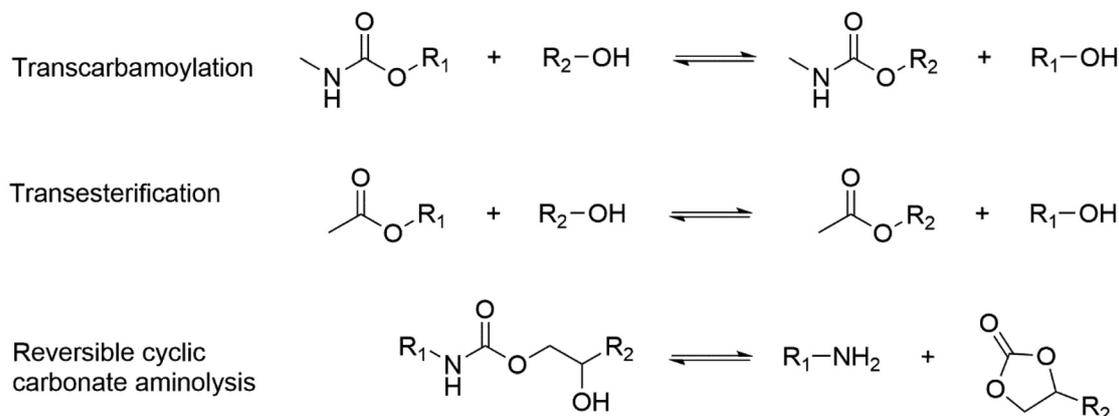
reactions.^{189,193,194} Reactions between carbamate or urethane groups and hydroxyl groups, essential for the reprocessing and recycling of NIPU and PHU, are termed transcarbamoylation or transurethanization. Urethane exchange specifically refers to reactions that do not involve interactions with hydroxyl



groups. Transcarbamoylation can occur *via* two mechanisms, dissociative (an elimination–addition mechanism involving bond breaking and reformation of alcohol and isocyanate moieties) or associative (an addition–elimination displacement mechanism).¹⁹⁵ Associative transesterification reactions and dissociative reversible cyclic carbonate aminolysis can also participate in rearranging the PHU structure during reprocessing (Scheme 13).¹⁹¹

Although conventional PU macromolecule reprocessing has been deemed inefficient and slow, requiring the use of appropriate catalysts, such as tin-based catalysts (dibutyltin dilaurate, DBTDL)¹⁸⁴ or 4-(dimethylamino)pyridine (DMAP), PHU networks are superior in their reprocessing ability due to the presence of primary and secondary hydroxyl groups, which can readily partake in carbamate exchange reactions (transcarbamoylation and transurethanisation) under catalyst-free conditions.^{52,55,194–197} The occurrence of reversible dissociative ring-opening/ring-closing of cyclic carbonate by amine, together with associative transcarbamoylation during PHU reprocessing ($T = 140\text{ }^{\circ}\text{C}$, $P \sim 10\text{ MPa}$ for 2 h), was discovered by Chen *et al.*¹⁹¹ in 2017 and confirmed in subsequent studies.¹⁹⁴ The occurrence of transesterification reactions was also confirmed by Hu *et al.*,¹⁸⁸ who reprocessed dynamic PHU networks synthesized from bio-derived carbonated soybean oil (CSBO) and sorbitol ether carbonate (SEC) with either a synthetic diamine or a bio-based diamine using compression molding at $T = 110\text{ }^{\circ}\text{C}$, $P \sim 11\text{ MPa}$ for 30 min. It was confirmed that transesterification reactions occur under these conditions but are relatively slow. Additionally, it was demonstrated that SEC-based PHU exhibited significantly worse reprocessability compared to CSBO-based PHU due to the higher functionality of groups responsible for cross-linking with short chains between adjacent groups, which led to steric effects and limited mobility of functional groups, both during synthesis and reprocessing. Purwanto *et al.*⁹⁷ reported studies on the reprocessability of flexible NIPU foams obtained from the reaction of cyclic carbonates, amines, and thiols. The NIPU foams were reprocessed three times by compression molding at $T = 160\text{ }^{\circ}\text{C}$, $P \sim 16\text{ MPa}$ for 3 h to produce recycled films.

DBU used in the foam synthesis process also acted as a catalyst during reprocessing. It was observed that during reprocessing, the unreacted cyclic carbonate was consumed, leading to a post-curing effect and an increase in the glass transition temperature of the film compared to the original NIPU foam. In subsequent work, the same authors reported the synthesis and reprocessing of NIPU foams based on CNSL-derived cyclic carbonates. Foam scraps were subjected to compression molding at $T = 140\text{ }^{\circ}\text{C}$, $P \sim 16\text{ MPa}$ for 2 h to produce recycled films.⁴⁵ Similarly, Detrembleur and coworkers⁵³ reported the reprocessability of water-blown self-blown NIPU foams owing to the presence of pending diols groups. Compression moulding was conducted at $160\text{ }^{\circ}\text{C}$ at 2 tons per cm^2 pressure for 2 h. Recently, Purwanto *et al.*⁹⁷ reprocessed bio-based NIPU foams into bulk films using compression molding at $T = 120\text{ }^{\circ}\text{C}$, $P \sim 10\text{ MPa}$ for 1 h. It was determined that the rearrangement of the PHU network was primarily driven by transcarbamoylation reactions, with contributions from transesterification and reversible cyclic carbonate aminolysis. However, it was found that at temperatures below $150\text{--}160\text{ }^{\circ}\text{C}$, transesterification is largely inactive or significantly suppressed, and only at temperatures above $180\text{ }^{\circ}\text{C}$ the active rearrangement of ester bonds occurred, allowing increased mobility in the PHU network to rearrange. Moreover, the presence of hydroxyl groups in the NIPU material backbone resulted in an increase its hydrophilicity, which may promote hydrolysis, and thus lead to a decrease in the mechanical performances. Monie *et al.*¹⁶⁷ explored the reprocessing of cross-linked network PHU foams into films or structural coatings through heat treatment. The obtained films presented integral structures (no cracks or holes were present), while preserving the crosslinked structures of the original foams. A second life to NIPU materials was then provided as coatings (combined with nylon films) for wear applications, closing the loop of the circular economy. Conclusively, in a recent study, Chen *et al.*¹⁹⁷ developed a series of NIPTU foams through catalyst-free synthesis. The highly dynamic disulfide crosslinks in these foams allow reprocessing by compression molding at temperatures between $140\text{ }^{\circ}\text{C}$ and $180\text{ }^{\circ}\text{C}$. NIPTU foams were also repro-



Scheme 13 Reversible cyclic carbonate aminolysis, transesterification and transcarbamoylation reactions.¹⁸⁸



cessed using extrusion and injection molding to reform the material and produce films. The self-healing properties of NIPTU foams were also validated. The reprocessing route is schematically shown in Fig. 9.

Overall, the presence of dynamic covalent bonds in polymer networks facilitates the reprocessability and potential reuse of the materials. However, several challenges must still be addressed.¹⁹⁸ For instance, CANs are mainly derived from petrol-based systems, although few emerging alternatives based on sustainable aromatic building blocks such as lignin, CNSL, tannins and others¹⁹⁹ have recently been reported in the literature. Another drawback is that incorporating CANs into the polymer matrix can reduce the mechanical performance of the material, making it more susceptible to deformations such as creep,^{200,201} a time-dependent deformation under constant stress, particularly at elevated temperatures below the reprocessing threshold. In contrast, conventional thermosets, characterized by permanent covalent cross-links, exhibit intrinsic resistance to creep.^{200,201} In the study by Hu *et al.*,²⁰² reprocessable PHU networks reinforced with polyhedral oligomeric silsesquioxanes (POSS) were examined for their creep resistance at elevated temperatures. The results indicated that these dynamic PHU networks exhibited minimal creep, comparable to permanently cross-linked materials at 80–90 °C (approximately 50–60 °C below the reprocessing temperature) under a constant 3.0 kPa shear stress. Indeed, the addition of POSS significantly enhanced the thermal stability of the material without affecting its creep behavior.

Despite their considerable potential, the challenges associated with CANs, make the technological transfer from laboratory to industrial applications impractical from both an economic and environmental perspective. The complexity of their

production process, reliance on petroleum-based systems, the potential reduction in mechanical performance, and difficulties in monitoring the reactivity of CANs during reprocessing all contribute to this challenge. As a result, the overall costs and technological hurdles prevent the scaling-up of these materials to industrial levels in the near future.

6. Environmental assessment of precursors and NIPU foams

The evaluation of the environmental impact and potential hazards of products and technologies is critical. Indeed, the mere use of sustainable chemical building blocks and renewable processes might not always guarantee higher levels of sustainability as well as reduced environmental impact of the large-scale production processes.¹¹ In this regard, Life Cycle Assessment (LCA) is a standardized and globally recognized methodology adopted by several companies and academic research units to estimate the environmental impacts according to well-defined parameters known as impact categories (ICs), such as global warming potential, GWP^{11,203} and eco and human toxicological indicators, such as freshwater aquatic ecotoxicity, FAETP, and human toxicity, HTTP, throughout its entire process, from the production of precursors to waste management.²⁰⁴

LCA analysis is regulated by two standards, ISO 14040 and ISO 14044, and involves a “cradle to grave” approach, which is devoted to investigating the life cycles of products and materials comprising the following stages: (i) extraction of raw materials, (ii) processing, (iii) transportation, (iv) usage, (v) waste disposal and (vi) recycling and re-use of waste materials as new raw materials.²⁰⁵ All these points are investigated

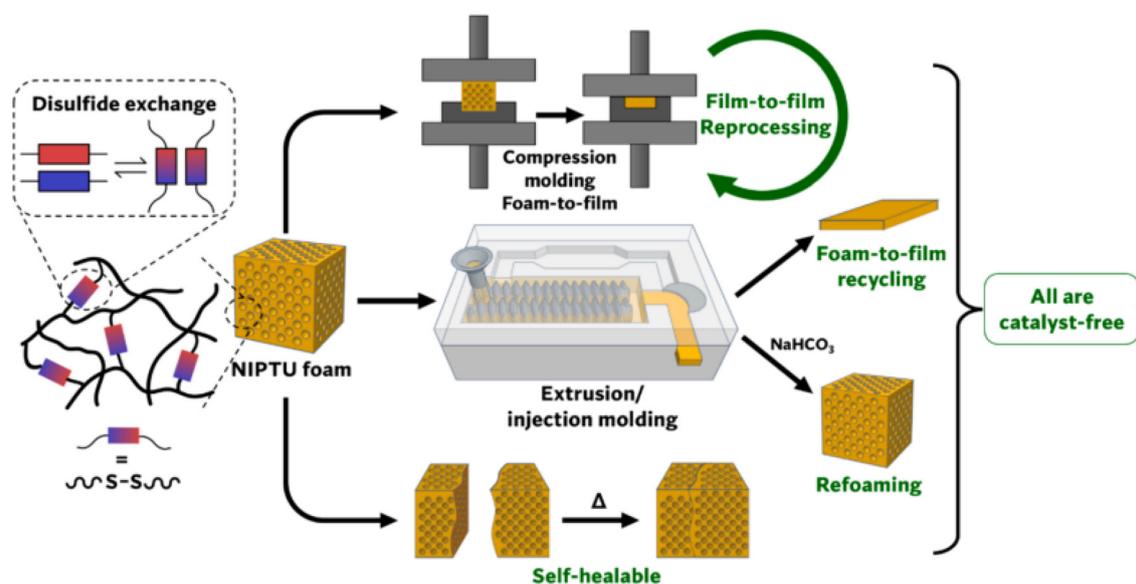


Fig. 9 Bio-based, catalyst-free non-isocyanate polythiourethane (NIPTU) foams characterized by dynamic chemical structure, fast reprocessability, extrudability and re-foamability. Reproduced from ref. 197, with permission from Elsevier Ltd., Copyright (2024). License number 6034210145754.



throughout the LCA main process, which is divided into four different phases. Briefly, the first phase is the definition of goal and scope, where the scope of the analysis is determined, including the product or process under study, the extent of the analysis, and the specific IC from the EN 15804 standard that will guide the assessment. The second phase involves the life cycle inventory (LCI), which entails collecting data on all the inputs such as raw materials and energy and outputs, including emissions to air, land, or water, related to the specific system to be analyzed. The third phase is the life cycle impact assessment (LCIA), where the collected data are used to quantify the environmental impacts of the product or the process. The impact is measured using indicators with corresponding equivalent units, such as carbon dioxide equivalents (CO₂-eq) for climate change, allowing an easier comparison of the impacts between different substances. Finally, the fourth phase is the interpretation of the data, where the results are analyzed to draw the conclusions. This step includes comparing the environmental performance of the products to similar products, identifying the opportunities for reducing the impact, and exploring the pathways to enhance the efficiency. To perform this comprehensive analysis regarding a single topic, sophisticated software is necessary, where most common ones are SimaPro™²⁰⁶ Gabi™,²⁰⁷ Ecochain Mobius™, OneClick LCA™,²⁰⁸ OpenLCA™¹¹ and Umberto.²⁰⁹

Owing to the environmental issues related to PU production, the development of NIPU foams as more sustainable alternatives to PU foams can be of pivotal interest in the field. Thus, a sustainability assessment of this new class of materials is noteworthy. However, the number of publications on the detailed LCA assessment of NIPU foams as well as regarding their economic feasibility is still extremely limited due to the partial data sets comprehending the raw materials, processes, and services involved in the production of NIPU foams. In addition, the sensitivity concerning the environmental issue represented by the use of di-isocyanates and translated into the studies of NIPU production was initiated approximately twenty years ago.²¹⁰ From a wider perspective, the introduction of NIPU-based materials on the market may have several environmental benefits, such as the total absence of solvents and the use of greener building blocks.²¹¹

6.1. Environmental assessment of precursors

Preliminary studies reported the environmental assessment of NIPU precursors, specifically about 5CCs. LCA analysis on CCs was mostly performed on that synthesized from captured CO₂, being proposed as a sustainable CC synthesis route, with a consistent reduction in the GWP parameter and the usage of fossil oil.²¹² EC was selected as a model precursor given that available data sets in the inventory for LCA are available, even if collected by processes conducted at a low Technology Readiness Level (TRL). As reported by Jahanbani,²¹³ the synthesis of EC involves the reaction between ethylene oxide and CO₂ at 120 °C and 16 bar. CO₂ was extracted from waste gas streams derived from other chemical processes, whereas the production of ethylene oxide was mainly based on bioethanol

from wood waste, together with an energy supply derived from renewable sources. The LCA was evaluated for GWP and human health as ICs. It was found that the best reduction of these two categories was achieved by involving the epoxide obtained from bio-ethylene oxide, and CO₂ captured with systems in which renewable energy was employed. On the contrary, the LCA evaluation of the synthesis of other NIPU precursors, *i.e.* carbamates or diamines, has not been reported in the open literature to date.

In the doctoral dissertation of C. M. Laprise,²¹⁴ an LCA was performed focusing on the epoxidation process, which is crucial for synthesizing epoxidized fatty oils (EFO) from natural oils such as methyl oleate (MO), oleic acid (OA), and fish oil (FO). This process is pivotal given that the resulting epoxides are used to prepare cyclic carbonates by reacting with CO₂, which react with amines to create NIPUs. It is evident that the LCA analysis was performed in conjunction with the four epoxidation processes explored, enabling a greener route to be selected for the production of the NIPU. Besides GWP, eight more ICs were selected including acidification potential (AP), ozone depletion potential (OD), smog formation potential (SFP), human toxicity by ingestion (INGTP) and inhalation (INHTP) potentials, persistence (PER), bioaccumulation (BIOACC), and abiotic resource depletion potential (ADP).

The analysis found that the method using 3-chloroperoxybenzoic acid (*m*-CPBA, Route 1) had the highest GWP at 800 units, mostly due to the heavy use of unpleasant toxic solvents, *e.g.* dichloromethane (CH₂Cl₂), which contributed to a high human toxicity potential and smog formation. This method was deemed the least “green”. The second and third routes considered the use of sulfuric acid (H₂SO₄) and choline chloride-oxalic acid (ChCl-OxA), respectively, together with the use of H₂O₂. These two methods resulted in much greener processes compared to Route 1, but they still had a significant impact, especially due to the use of corrosive acids and the high inhalation and ingestion indices due to the use of hydrogen peroxide, yielding a GWP of 192 and 133, respectively. However, in the fourth method, H₂O₂ was maintained and used with formic acid (HCOOH), which made Route 4 the greenest option, with the lowest global warming potential of 54 units, with no acidification, and with low toxicity levels. This route had a high efficiency and minimal environmental impact, making it the most promising for sustainable epoxidation. Additionally, using dimethyl carbonate (DMC), obtained in an eco-friendly way²¹⁵ as a solvent further improved the green profile by replacing CH₂Cl₂.

6.2. Environmental assessment of NIPU materials

Liang and co-workers²¹⁶ conducted an accurate LCA and techno-economic analysis of the production and reprocessing of NIPU and NIPTU foamed materials using data from patents, the open literature, and their experiments. Focusing on LCA, they selected three ICs, namely greenhouse gas (GHG) emissions, use of fossil energy, and water consumption, to conduct the analysis on PHU, NIPTU, and the reprocessed NIPUs. These data were compared to the same metrics with conven-



tional PU. The study considered bulk materials, not foams, but provided useful information about the nature and the weight of each NIPU precursor on the final LCA analysis. This study did not include concerns regarding the use of blowing agents, which would have shown a substantial increase in GHG emissions and the use of fossil energy, even if cyclopentane alone was included. However, they analyzed four different NIPU production pathways, as follows: (1) biomass-based PHU, (2) second-generation PHU *via* depolymerization, (3) biomass-based NIPTU, and (4) second-generation NIPTU *via* depolymerization (Fig. 10). As a result, the water and fossil energy use were significantly higher for both the virgin PHU and NIPTU production than for their traditional counterpart, while the GHG emissions were lower for PHU production and narrowly higher for NIPTU. Concerning the reprocessing of both PHU and NIPTU, the water usage was significantly higher with respect to the traditional PU foams and virgin PHU and NIPTU, use of fossil energy, and GHG emissions decreased to a lower amount, depending on whether PHU or NIPTU were involved. The value of the LCA analysis lies in its ability to identify the key material input parameters that have the greatest impact on the selected ICs. This insight enables the authors to provide clear guidance on optimizing the production process to align with the desired sustainability goals of the final products. Given that XDA was selected and fossil-based methanol was replaced with bio-methanol, one-third of the fossil energy use was saved, decreasing with respect to the traditional PU foam production. Moreover, a 16% reduction in fossil energy use could be achieved in the NIPTU production if

xylene was recycled. The same authors conducted for the first time a TEA assessment of the resulting NIPU foams. Understanding the economic viability of NIPU foams is essential for assessing their potential impact on the current market. Thus, a sensitivity analysis was carried out to identify cost items, such as taxes, operating expenses, fixed costs, utilities, and raw material costs. The authors reported that the minimum selling price (MSP) of NIPU, PHU, and second-generation PHU foams could be lower than or comparable to that of conventional petroleum-based flexible foams, which serve as a cost benchmark in the range of 3.5–4.5 USD per kg. However, achieving cost competitiveness largely depends on the careful selection of raw materials, such as diamines and solvents used in foam reprocessing (*e.g.*, THF), which significantly influence the material costs. Furthermore, optimizing the design of pilot or industrial-scale production facilities is recommended to align operating costs with that of existing polyurethane (PU) manufacturing lines. Nevertheless, as a main result of this preliminary study, the authors found that from an economic point of view, the best option was to reprocess NIPU foams, in agreement with the circular economy perspectives.

Concerning NIPU-based foams, the evaluation of the environmental profile of lignin-based NIPU foams has been reported by Sternberg & Pilla.¹⁶² The main topic was the evaluation of the energy consumption and GWP of both virgin foam production (first generation) and chemical recycling process (second generation). The authors compared several ICs of both generations of NIPU foams. In the production of first-gene-

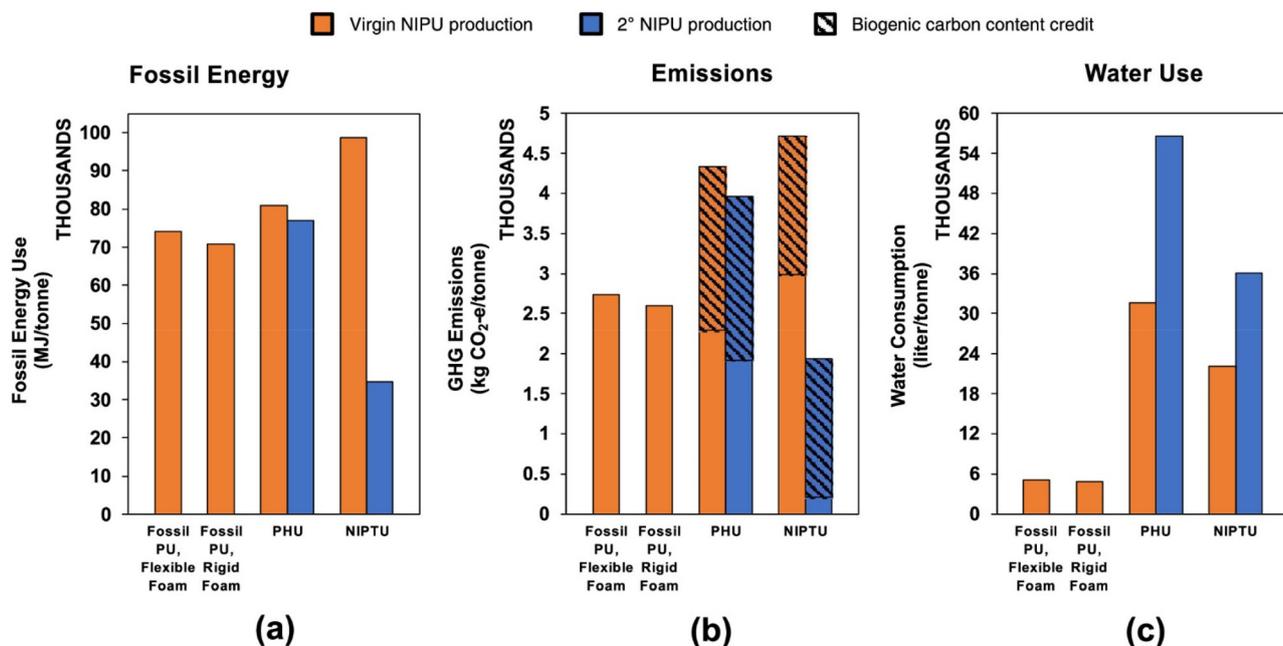


Fig. 10 Impact categories of different NIPU foams: (a) fossil energy consumption, (b) GHG emissions, and (c) water consumption impacts of NIPU production and reprocessing. Impacts for PHU and NIPTU production are compared with the production of PU flexible and rigid foams. Orange bars are representative of PU/NIPU production, and blue bars are representative of NIPU reprocessing. Reproduced from ref. 216 with permission from the American Chemical Society, Copyright (2024). Licensed under CC-BY-NC-ND 4.0.



ration NIPU foam, the recycling process was performed with different NIPU: solvent ratios of 10% and 20%. The GWP of the recycled NIPU was three times higher than that of the first-generation NIPU, given that low loading ratios (10% NIPU: solvent) were used. However, by increasing the loading ratio to 20%, the GWP index of the recycled NIPU was reduced, making it only 47% higher than its first-generation counterpart. If industrial process steam was used instead of electricity, a 17.6% reduction in GWP was registered, bringing the GWP of the recycled NIPU much closer to the first-generation value. If process steam was used for the total energy demand, it might have decreased by around 26%. Additionally, using the appropriate amount of ethylene glycol (EG) in the recycling process could potentially decrease the environmental impacts even further, *i.e.* a 5% EG mixture in the solvent could decrease the GWP of recycled NIPU below the first-generation value.¹⁵⁹ Nevertheless, given that the LCA was based on hypothetical scaled-up laboratory procedures, it indicated that with further optimization on a factual industrial scale, the chemical recycling process can achieve even lower environmental impacts than indicated by the initial laboratory results.

7. Conclusions and future perspectives

Over the last decade, non-isocyanate polyurethane (NIPU) foams have gained considerable attention as alternatives to isocyanate-based PU foams owing to the chief environmental concerns associated with isocyanate compounds. These materials provide interesting features compared to the conventional PU systems, such as a unique structure characterized by an abundance of hydroxyl groups in the polymer backbone, which makes them fully recyclable and reprocessable. NIPU foams can be synthesized by two main environmentally friendly routes, *i.e.* transurethanization of carbamates with alcohols, and aminolysis of linear or cyclic carbonates with diamines. The building blocks of NIPU foams can be produced *via* different reactions and from various renewable and waste sources, such as vegetable oils, lignin, terpenes, and sugars.

In this review article, a comprehensive analysis on the synthesis of NIPU foams is provided, from the synthesis of the bio-based precursors to the environmental (Life Cycle Assessment, LCA) and techno-economic (TEA) assessment of the production processes and final materials. Particular attention was dedicated to the blowing routes, which can be roughly divided into two main categories, non-self-blowing (where physical BAs are employed) and self-blowing routes (consisting of endogenous reactions such as decarboxylation of 5 CCs *via* S-alkylation, hydrolysis or *via* suitable chemical BAs). The chemical, physical, mechanical, and thermal characteristics together with the potential applications of the resulting foams were discussed herein. To improve the exothermicity, and thus let the synthesis be conducted at room conditions and at relatively short reaction times (5–30 min), an intriguing and promising way based on epoxy reactions has

been set up by the recent literature. Although LCA and TEA analyses have been poorly investigated in the NIPU foam field, preliminary efforts proved the potential economic feasibility of the current routes for NIPU foams as well as the reduced environmental impacts. This gives hope to boost their market in the next few years, leading to potential replacement of the conventional PU materials in several applications. Nevertheless, future investigations are required to examine these routes as well as to exploit different bio-based precursors as well as solid fillers to enhance the final performances of the resulting materials. Compared to isocyanate-based PU foams, NIPU foams have been indicated as fully reprocessable materials owing to the presence of OH or SH functional groups, which can promptly take part in carbamate exchange reactions, either with the aid of specific catalysts or under catalyst-free conditions. As a result, the materials can undergo self-healing or even complete reshaping, providing a valuable solution for the end-life management of thermosetting PU-based systems. Conclusively, efforts should be made in the near future to address the hydrophilicity of these materials through the use of dedicated additives or fillers, and thus by accurately optimizing foam formulations.

Possible future research should address the upcycling of NIPU foams, by reintegrating NIPU foam scraps as building blocks for new-generation materials. Contextually, the evaluation of the environmental impact of NIPU precursors and foams through LCA and TEA should be investigated more extensively. Detailed insights into each stage of the life cycle of foam, from the selection of the building blocks to the end-of-life phases, should be provided, highlighting potential environmental impacts at each step.

Abbreviations

ADP	Abiotic depletion potential
AIBN	Azobisisobutyronitrile
AOPHA	Amine-terminated oligomer phenylhydroxylamine
AP	Acidification potential
BA	Blowing agent
BCI	Bis-carbonyl imidazoline
BIOACC	Bioaccumulation
Bis AEE	1,2-Bis(aminoethoxy)ethane
Br ⁻	Bromide ion
CAGR	Compound annual growth rate
CANs	Covalent adaptable networks
CC	Cyclic carbonate
C.	<i>Corynebacterium glutamicum</i>
glutamicum	
CH ₂ Br ₂	Dibromomethane
CH ₂ Cl ₂	Dichloromethane
ChCl–OxA	Chloride–oxalic acid
Cl ⁻	Chloride ion
CLSO	Carbonated linseed oil
CMR	Carcinogenic, mutagenic and reprotoxic



CNSL	Cashew nutshell liquid	INHTP	Inhalation toxicity potential
CO ₂	Carbon dioxide	IPDA	Isophorone diamine
CO ₂ -eq	Carbon dioxide equivalent	ISO	International standard organization
CSBO	Carbonated soybean oil	K ₂ CO ₃	Potassium carbonate
CS ₂	Carbon disulfide	KOH	Potassium hydroxide
CTC	Cyclic dithiocarbonate	LC	Linear carbonate
DA	Dimeric acid	LCA	Life cycle assessment
DAB	1,4-Diaminobutane	LCI	Life cycle inventory
DABCO	Diaminobicyclooctane	LCIA	Life cycle impact assessment
DAP	1,5-Diaminopentane	LiBr	Lithium bromide
DBN	1,5-Diazabicyclo(4.3.0)non-5-ene	LOI	Limiting oxygen index
DBTDL	Dibutyltin dilaurate	<i>m</i> -CPBA	3-Chloroperoxybenzoic acid
DBU	1,5-Diazabicyclo(5.4.0)undec-7-ene	MDI	Methylene-diphenyl di-isocyanate
DCM	Dichloromethane	MDXA	<i>N</i> -Methyldiethanolamine
DCPN	Dynamic covalent polymeric network	MetOH	Methanol
DEC	Diethyl carbonate	MO	Methyl oleate
DMAP	(Dimethylamino)pyridine	MSP	Minimum selling price
DMC	Dimethyl carbonate	NaHCO ₃	Sodium bi-carbonate
DMF	Dimethyl formamide	NAHcT	<i>N</i> -Acetylhomocysteine thiolactone
DMSO	Dimethyl sulfoxide	NCO	Isocyanate functional group
<i>E. coli</i>	<i>Escherichia coli</i>	NH ₂	Amino group
EC	Ethylene carbonate	NIPU	Non-isocyanate polyurethane
EDT	Ethane-1,2-dithiol	NITPU	Non-isocyanate polythiourethane
EFO	Epoxidized fatty oil	OA	Oleic acid
EG	Ethylene glycol	OD	Ozone depletion potential
EOBPA	Bisphenol A diglycidyl-ether	OH	Hydroxyl group
EO-TMPTC	Ethoxylated trimethylolpropane triglycidyl carbonate	O ₂	Oxygen
EO-TMPGC	Ethoxylated TMPTC derivatives	PC	Propylene carbonate
ESBO	Epoxidized soybean oil	PDMS	Polydimethylsiloxane
EtOAc	Ethyl acetate	PEG	Polyethylene glycol
FAETP	Fresh water aquatic ecotoxicity	PER	Persistence
FBC	Furan bis(cyclic carbonate)	PHU	Polyhydroxy urethane
FO	Fish oil	pMC	Percent modern carbon
GC	Glycerol carbonate	PMHS	Polymethyl-hydrogen siloxane
GHG	Greenhouse gas	POSS	Polyhedral oligomeric silsesquioxanes
GTC	Glycerol tricyclic carbonate	PPO-Bis-C ₅	Polypropylene oxide bis-carbonate
GTE	Glycerol triglycidylether	PPOBC	Poly(propylene oxide) bis-carbonate
GWP	Global warming potential	PU	Polyurethane
HBD	Hydrogen-bond donors	RDGCC	Resorcinol diglycidyl ether cyclic carbonates
HC	Hydrocarbon	REACH	Regulation on registration, evaluation, authorisation and restriction of chemicals
HCl	Chloride acid	RIM	Reaction injection molding
HCOOH	Formic acid	ROH	Alcohol
HFC	Hydrofluorocarbon	RT	Room temperature
HFO	Hydrofluorolefine	<i>S. aureus</i>	<i>Staphylococcus aureus</i>
HMDA	Hexamethyldiamine	SC	Sodium carbonate
HMF	Hydroxymethylfurfural	Sc-CO ₂	Supercritical carbon dioxide
HTTP	Human toxicity	SEC	Sorbitol ether carbonate
HX	Halide acid	SEM	Scanning electron microscopy
H ₂	Hydrogen	SFP	Smog formation potential
H ₂ O	Distilled water	<i>T</i>	Temperature
H ₂ O ₂	Hydrogen peroxide	TADE	3,3,4,4-Tetraaminodiphenyl ether
H ₂ S	Hydrogen sulfide	TBAB	Tetrabutylammonium bromide
I ⁻	Iodide ion	TBAC	Tetrabutylammonium chloride
IC	Impact category	TBAI	Tetrabutylammonium iodide
INGTP	Ingestion toxicity potential	TBD	Triazabicyclodecene



$T_{d,5\%}$	Degradation temperature at 5% weight loss variation
TDI	Toluene di-isocyanate
TEA	Techno-economic analysis
TETA	Triethylenetetramine
TEGDT	3,6-Dioxa-1,8-octanedithiol
THF	Tetrahydrofuran
THFDM	2,5-bis(hydroxymethyl)tetrahydrofuran
T_g	Glass transition temperature
T_m	Melting temperature
TMP	Tri-methyl propane
TMPE	Trimethylolpropane triglycidyl ether
TMPTC	Trimethylol propane triglycidyl carbonate
TMP-Tri-C ₅	Trimethylolpropane tris-carbonate
TNIPU	Tannin based-non isocyanate polyurethane foams
TRL	Technology readiness level
VOC	Volatile organic compounds
USD	United States Dollar
XDA	<i>m</i> -Xylylenediamine
Y	Lanthanide salt
(NO ₃) ₃ ·6H ₂ O	
1,3-BAC	1,3-Bis(aminomethyl)cyclohexane
5CC	5-Membered ring cyclic carbonate
6 CC	6-Membered ring cyclic carbonate
7CC	7-Membered ring cyclic carbonate
8CC	8-Membered ring cyclic carbonate

Greek symbols

ρ	Apparent density
λ	Thermal conductivity
σ (40%)	Compressive strength at 40% deformation
σ^*	Specific compressive strength

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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