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Advances in bio-based non-isocyanate polyurethane-acrylate: Synthesis and durability

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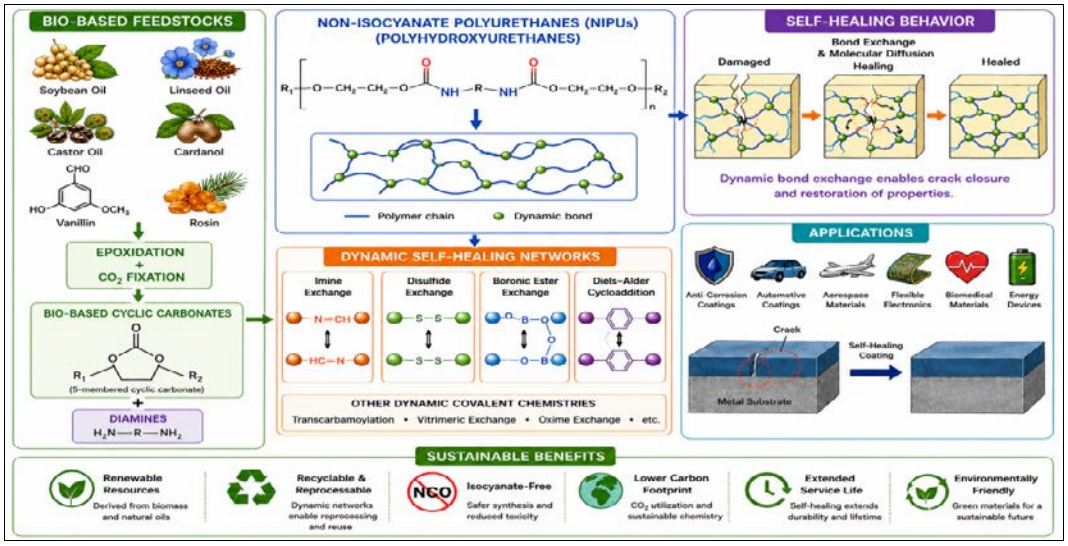
Abstract
The growing concern for toxic isocyanate emissions and increasing regulations are driving the development of non-isocyanate polyurethane (NIPU) products as safe and eco-friendly replacements for traditional polyurethane products. One of the emerging strategies for developing NIPUs is combining NIPU chemistry with acrylate functionalities to develop non-isocyanate polyurethane-acrylate (NIPUA) hybrid networks which offer a green synthesis method combined with quick curing capabilities and excellent coating properties. In this review we provide an overview of recent developments in the bio-based synthesis of NIPUs using vegetable oils-derived cyclic carbonates that can be transformed into acrylate functional systems by post-modification, pre-functionalized monomers, or hybrid addition strategies. We emphasize the relationship between structure and properties that affect curing behaviour, cross-linking density, tensile strength, adhesion and chemical resistance in NIPUA coatings. We discuss in detail how CO_2 utilization, water-borne formulation, UV curing and the emerging area of dynamic covalent chemistry will improve both the sustainability and functionality of NIPUA coatings. Finally, we outline our vision for the future towards fully bio-based, self-healing, water-borne NIPUA coatings based on circular economy principles and advanced manufacturing technologies, including additive manufacturing and smart protective surfaces.

Graphical Abstract



Keywords: Non-isocyanate polyurethane (NIPU), polyurethane–acrylate hybrid networks, bio-based coatings, cyclic carbonate polymerization, self-healing materials, waterborne coating systems

Introduction
Polyurethanes (PUs) are an extremely versatile family of polymers utilized in a variety of applications including coatings, foams, sealants and adhesives. Their ability to provide promising performance characteristics along with their extensive use has led to the need for alternative, greener methods of synthesizing PUs that will replace the currently used toxic isocyanates. Isocyanates are hazardous chemicals that pose a risk to human health through respiratory sensitization and create ecological damage through their toxicity in ecosystems. Polyurethane is consumed globally in excess of 20 million tons per year, primarily utilizing diisocyanates that include toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), both of which are derived from hazardous phosgene intermediate sources [1, 2]. A major driver behind the transition to greener, safer polyurethane formulations was a result of the increased regulatory emphasis of environmental agencies and the growing movement towards "green" chemistry. The EU REACH directive and OSHA have established guidelines and standards to limit exposure to isocyanate compounds; therefore, there has been increasing interest in developing environmentally acceptable and safe polyurethane formulations that meet the principles of green chemistry [3, 4]. Non-isocyanate polyurethane (NIPU) has

emerged as a new class of environmentally benign polymers that do not utilize hazardous isocyanates. NIPUs are produced by the reaction of amines and cyclic carbonates through a polyaddition mechanism that produces polymers with similar physical and chemical properties to those produced by traditional polyurethane synthesis [5]. The NIPU production method is inherently atom efficient, solvent free, and produces polymers containing pendant hydroxyl groups capable of forming hydrogen bonds and providing active sites for further modifications [6]. Therefore, NIPU production does not require isocyanates and consequently eliminates many of the safety concerns associated with their use, reduces the environmental impact of their production, reduces Volatile Organic Compound (VOC) emission [6, 7], and may provide economic advantages [5]. The NIPU production method is solvent and catalyst free, occurs under mild conditions and is atom-economical with no by-product formation. Additionally, CO_2 is a readily available source of cyclic carbonates through its cycloaddition reaction with epoxidized vegetable oils. Therefore, the NIPU production method is linked to carbon capture and utilization strategies that support circular economy objectives [5, 8, 9]. Vegetable oils offer numerous benefits as renewable feedstock's in addition to providing a high level of unsaturation that is conducive to the sequential epoxide ring opening (carbonation) and amine reaction used in forming soft segments of many commercially available bio-NIPUAs. Vegetable oil derived fatty acid chains can be obtained at a very competitive price compared to other potential renewable chemical feedstock's. Also, vegetable oils are abundant in nature. Therefore, vegetable oils are an ideal choice as a renewable feedstock for the development of sustainable NIPU systems [5, 7]. Additionally, renewable chemical feedstocks such as vegetable oils provide several other benefits over traditional fossil fuel based chemical feedstocks. First, use of these types of feedstocks will help to decrease our reliance on fossil fuels by allowing us to use alternative renewable resources. Second, these types of chemical feedstocks produce fewer volatile organic compounds (VOCs) than fossil-fuel derived chemical feedstocks. Third, production of products using renewable feedstocks produces less carbon dioxide per unit mass of product produced when compared to products made from fossil fuels [12]. Vegetable oils contain a wide range of functional groups that allow for the precise control of structure and molecular architecture of the resulting polyurethane products making them ideal precursors to high-performance, biodegradable polyurethane [12, 13]. The versatility of vegetable oil based NIPUs has been demonstrated by Rayung *et al*. and Sulthana *et al*. who have shown the applicability of NIPUs to coatings, corrosion protection, and fouling prevention [5, 14]. Advances in the efficiency of CO_2-epoxide cycloaddition reactions using ionic liquids and metal-free catalysts have greatly improved the scalability and eco-friendliness of the cyclic carbonate production processes [15]. Although advances have been made in the areas of scalability and efficiency of the production of NIPUs, NIPU coatings continue to suffer from slow curing times, low hardness and insufficient crosslink density limiting their utility in industrial applications. These limitations arise from the secondary hydroxyl groups present in the hydroxyurethane linkages within the NIPUs. Hydroxyurethane linkages exhibit much reduced reactivity toward cross-linking agents when compared to isocyanates; thus creating challenges in achieving high-density cross-linked films and rapid curing [4, 16].

Transition from PU to NIPU–Acrylate

1. Conventional Polyurethane (PUs).

PUs are generally formed by polyaddition of polyols to isocyanates, forming urethane (-NH-CO-O-) bonds and are typically classified as step-growth polymers. The formation of morphology and resultant properties of PUs are influenced by the proportion of hard (isocyanate-rich) and soft (polyol-rich) phases, influencing their mechanical strength, flexibility and chemical resistance [17]. While there are many benefits associated with PUs, there remain many challenges to overcome within the production processes, particularly concerning their toxicity and hazardous precursors. There are a number of concerns regarding the side reactions involved in the synthesis of PUs and the utilization of phosgene; a highly toxic precursor for isocyanates. Phosgene is extremely toxic and therefore hazardous to handle and produce and results in health and environmental pollution [6]. Furthermore, they are toxic due to the high reactivity of the -N=C=O group of isocyanate monomers and they contribute significantly to the PU industry [1, 18]. One of the primary isocyanates used in the PU industry, classified as carcinogenic, mutagenic and reproduction toxic (CMR) are toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) and diphenylmethane diisocyanate (MDI) [19]. Occupational asthma, respiratory inflammation and lung cancer can be caused when these substances are inhaled or absorbed into the skin and therefore represent serious health risks. As a result of the toxicity of isocyanates based on phosgene chemistry and the emission of volatile organic compounds (VOCs), safer and more sustainable alternative alternatives are being developed [20]. The fig. 2 demonstrates the standard mechanism of forming a urethane from the reaction of a polyol with isocyanate and indicates the chemical basis of the formation of a urethane linkage in traditional polyurethane systems. Although this method has been very effective for developing coatings with high performance mechanically and as coatings, it is still dependent upon toxic isocyanates and dangerous, environmentally hazardous intermediate compounds such as those derived from phosgene [6].

2. Non-Isocyanate Polyurethanes (NIPUs)

Instead of being made with isocyanates, the non-isocyanate polyurethanes (NIPUs), also known as poly(hydroxyurethane)s, use cyclic carbonates to react with the amines, producing 4-hydroxyurethane linkages [21]. This way of making NIPUs avoids the use of phosgene and utilizes CO_2 for cyclic carbonate formation [9]. Due to the presence of hydroxyl pendant groups, NIPUs show improved adhesion [22], however they often display increased viscosity and lower molecular weight than isocyanate-based polyurethanes [7]. The research has focused on the catalytic acceleration through quaternary ammonium salts, ionic liquids and metal oxides to overcome kinetic limitations [23, 24]. Bio-based NIPUs are created from vegetable oils such as soybean, linseed and jatropha [22]. They are epoxidized and carbonated with CO_2 to form multifunctional carbonated cyclic epoxides that are then polymerized with diamines to

give hydroxyurethane networks [5, 25]. These systems provide excellent adhesion and environmental resistance properties, and this is why there is an increasing interest for using them in coatings and adhesives [26]. NIPUs can be prepared by several methods. There are four main ways to prepare NIPUs, including polyaddition, polycondensation, ring-opening polymerisation, and rearrangement [7]. Fig. 1 illustrates the synthesis process of vegetable oil-based cyclic carbonates by epoxidation and subsequent carbonation with CO_2. It is also considered an important environmentally friendly route to prepare the green cyclic carbonate monomers that are primarily used in NIPU synthesis [5, 9]. The use of vegetable oils (renewable feedstocks) and CO_2 (a waste gas from many industrial processes), will make the production of polyurethane much more environmentally sustainable than using petrochemicals as feedstocks.

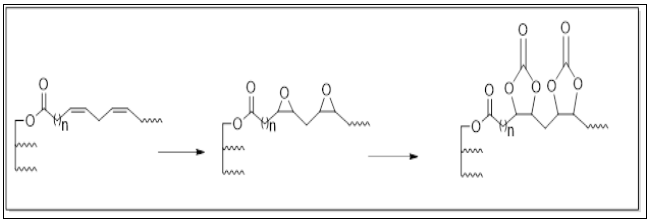


Fig 1: Synthesis pathway of vegetable oil-based cyclic carbonate (Redrawn based on literature reports).

2.1 NIPU Synthesis through polyaddition of Amines and Cyclic Carbonates.

The basic method for synthesizing non-isocyanate polyurethanes (NIPUs) involves a reaction of cyclic carbonates (CCs) with amines; both reactants have at least three complementary reactive sites. In addition to forming a urethane linkage, each reaction of CCs with amines produces a primary or secondary hydroxyl group as well; therefore, the NIPUs are sometimes referred to as polyhydroxyurethanes (PHUs) [16]. Lately, the preparation of NIPUs through reactions involving cyclic carbonates and amines has been very prominent among researchers searching for a sustainable approach to replace the traditional methods based on isocyanates [27, 28]. Cyclic carbonates possess many desirable properties that make them good candidates for a variety of applications. They exhibit high solubility, high boiling points, and great chemical versatility and can react with various functional groups such as aliphatic or aromatic amines, alcohols, thiols and carboxylic acids [7, 29]. Their biodegradability and lower toxicity compared to isocyanates is also attractive features for developing a more "green" polymer.

2.2 Polycondensation

The second method for forming polymer is known as polycondensation (transurethane reaction) [30]. The formation of non-isocyanate polyurethanes (NIPUs) through a transurethane reaction between a polycarbamate and a polyol is another alternative; however, it is viewed as being less environmentally acceptable due to the fact that polycarbamates are typically produced using phosgene [6, 31]. Additionally, green methods of producing NIPUs have been developed via a polycondensation reaction of a di- or multi-functional carbonate with a diamine, thus requiring no intermediate toxic agent [9]. Green alternatives to the production of polycarbamates include: the utilization of nitro precursors; oxidative aminolysis of amines; and urea-based reactions [32]. Urease has been alcoholized with many different catalysts [6]. Fig 5 summarizes the polycondensation approach for NIPU synthesis involving polycarbamates or polycarbonates and diamines. Although this method avoids direct isocyanate usage during polymer formation, certain precursor synthesis routes may still involve toxic intermediates, limiting the overall sustainability of the process [6, 33].

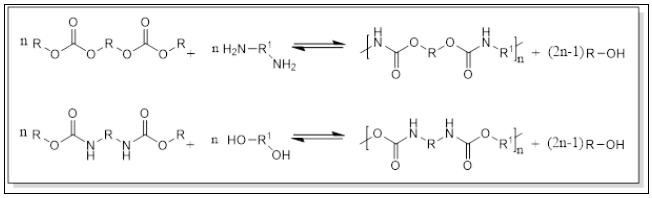


Fig 2: Pathway of acquisition of NIPU through polycondensation of polycarbamate and diol or polycarbonate and diamine (Redrawn based on [34])

2.3 Ring-Opening Polymerization

Another way to make NIPUs is through the ring-opening of six- and seven-membered carbamate rings [7]. This process is sensitive to temperature (best yields occur when the temperature is about 200°C), and is generally carried out using an assistive agent such as sodium hydride or N-acetylcaprolactam [7]. Although there has been considerable effort placed toward developing more environmentally-friendly methods for preparing cyclic carbamates, most of the current literature continues to describe the use of phosgene; therefore, the environmental impacts from producing NIPU are very similar to those associated with the production of polyurethane via traditional routes [3, 35] .

2.4 Rearrangement

To synthesize NIPUs, many different types of rearrangement reactions can be used for example, Curtius, Hofmann, and Lossen rearrangements. However, this method does not always reduce the toxicity of the end product relative to traditional methods since these reactions form isocyanates as intermediate products [5]. Additionally, the use of halogenated reagents (particularly bromine and chlorine) increases the amount of hazardous waste generated [36]. The most recent alternative to traditional Lossen-type rearrangement has been developed using non-toxic reagents by utilizing dimethyl carbonate as an activator in methanol, with a tertiary amine catalyst [16, 37]. As an example of how the lossen-type rearrangement has been advanced to provide less detrimental effects on the environment through the reduction of the reliance upon hazardous materials; it is important to continue to investigate truly isocyanate-free synthetic pathways [38]. Therefore, ongoing investigations will continue to develop new synthetic methods that completely avoid isocyanate formation, as an example; the direct polyaddition between bicyclic carbonates and diamines has successfully avoided the production of toxic materials and by products [38, 39].

3. NIPU–Acrylate Hybrids(NIPUA)

Although the NIPUs are safer and more eco-friendly, they are cured too slowly to become the standard in industry [25]. Therefore, it is necessary to combine NIPUs with acrylic to

create NIPU-Acrylic (NIPA) systems, which cure quickly under ultraviolet light (UV) or heat, and have higher cross-linking densities compared to other hybridized systems [25, 40]. There are two types of NIPU-Acrylic hybrids; one uses a 2-hydroxyurethane backbone which contains acrylate end groups allowing rapid curing and cross-linking densities, while the other type synthesized by Villa et. al., utilizes glycerol carbonate (meth) acrylates to act as both NIPU precursor and photo-reactive monomer for solvent free coating processes [41]. These NIPU-Acrylic hybrids appear to provide a viable means of addressing many of the disadvantages of traditional NIPUs, such as slower curing rates, and lower mechanical properties, enabling them to be applied to an array of industries, such as, high performance coatings, adhesives, etc [12, 40]. Wang *et al*., demonstrated that photosensitive NIPA resins may also be used in three-dimensional (3-D) printing, and their mechanical strength, biocompatibility, and curing rate were superior to those of commercial methacrylate systems [21]. The amine-acrylate chemistry of cyclic carbonates allows the development of versatile, environmentally friendly, and rapidly curing coatings [42].

Table 1: Various components of bio-based non-isocyanate polyurethane–acrylate (NIPU–Acrylate) formulation

Components	Effect / Inclusion	Ref.
Epoxidized vegetable oils (e.g., epoxidized mahua, soybean, linseed, castor, cardanol oils)	Serve as renewable precursors for cyclic carbonate synthesis; introduce long aliphatic chains for flexibility.	[5,17, 43]
Cyclic carbonates (derived from epoxidized vegetable oils)	Key isocyanate-free intermediates that react with amines to form hydroxyurethane linkages in NIPUs.	[16, 33, 39]
Diamines/polyamines(e.g.,ethylenediamine, diethylenetriamine, tris(2-aminoethyl)amine)	React with cyclic carbonates forming urethane linkages; control crosslink density and mechanical strength.	[28]
Acrylic monomers/resins(e.g., butyl acrylate, methyl methacrylate, hydroxyethyl acrylate)	Introduce the hard acrylate phase in hybrid NIPU–acrylate systems; enhance hardness, gloss, and chemical resistance.	[43]
Catalysts (e.g.,triethylamine,TBD, organocatalysts, DBTDL)	Accelerate cyclic carbonate synthesis and curing reactions under mild conditions.	[44]

Table 1 lists the main components and synthesis methods of Bio-Based NIPUA coating systems that include cyclic carbonate precursors, diamine monomers, acrylic additives, catalysts, and renewable feedstock materials. The comparisons of formulations provide a better understanding of how the choice of formulation can affect the performance characteristics of coatings, sustainability, and curing behaviours.

Acrylation approaches to make NIPU-Acrylate hybrids

Poly (hydroxyurethane), referred to as NIPU, prepolymer to acrylate-functional non-isocyanate polyurethane-acrylate (NIPUA) systems, is an important step toward the development of green chemistry in the area of polymer synthesis and high-performance coatings. Radical or photopolymerizable acrylated modification increases cross-link density, mechanical properties, and chemical durability by incorporating the radical or photopolymerizable vinyl functional groups into the polymer structure [45]. These modifications can be categorized into three types:

1. Post-polymerisation modification of NIPU prepolymers;
2. Pre-functionalized cyclic carbonate monomers;
3. Hybrid or addition methods.

1. Route 1-After NIPU Prepolymers Modification.

In this pathway, the NIPU backbone is first synthesized and the pendant hydroxyl groups (R -OH) are reduced to acrylate [22]. There are two primary sub-approaches, namely: (a) the use of esterification with (meth) acrylic reagents and (b) grafting with glycidyl methacrylate (GMA).

a. Esterification with (meth)acrylic reagents

Nucleophilic acylation of terminal and side chain hydroxyl functionalities on methacrylate ester polymers can occur rapidly when reacted with methacrylic anhydride (MAAH) or acryloyl chloride under mild temperature (0-40°C) in the presence of a tertiary amine base or 4-dimethylaminopyridine (DMAP) [33]. The reaction provides efficient formation of acrylate functionalities from hydroxyl functionalities, thereby providing reactive sites for subsequent UV-initiated photopolymerizations that enhance physical properties of the resultant materials [45]. Schimpf *et al*. demonstrated the synthesis of multifunctional polyhydroxyurethane methacrylates (HUMA) through reaction with methacrylic anhydride (MAAH) under conditions that resulted in high conversions and high-strength films. Successful acrylation was confirmed through spectroscopic analysis of FT-IR and ^{1}H-NMR data following the reaction. (-OH; 3400 cm $^{-1}$; -C=O; 1735 cm $^{-1}$; -CH=CH2; 5.6-6.2 ppm). The partial acrylation of NIPU (50/70%) allowed for retention of residual hydroxyl functionalities for adhesive purposes and provided cross-linking density to provide hardness and solvent resistance. Therefore, it is critical to maintain stoichiometric control during the acylation reaction; excessive anhydride and/or prolonged reaction times may result in excessive acrylation and brittle materials. Alternatively, acryloyl chloride can be employed to react with hydroxy-terminated NIPU oligomers under anhydrous conditions and at low temperatures, followed by removal of reaction by-products via purification steps]. In addition to anhydride and chlorides, another common method for acrylation of hydroxy-functionalities employs the reaction of methacrylic acid with NIPU polyols in the presence of a catalytic amount of an acidic compound, such as p-toluene sulfonic acid (p-TSA), and a free radical inhibitor to prevent premature polymerization [25].

b. The GMA grafting through epoxide ring-opening / transesterification.

The beginning of the type-A, less aggressive type of reaction of GMA with hydroxyl groups is typically accomplished through ring opening of an epoxide or transesterification. Utilizing a base as a catalyst, such as DBU or tertiary amines. In addition, butylated Hydroxytoluene (BHT) is added to inhibit polymerization of the PHU backbone. This method has been utilized by Ecochard *et al*. to produce hybrid PHUs that demonstrated superior mechanical properties of adhesion and flexibility

compared to those produced through MAAH esterification. The formation of etherified bonds involving the 5-hydroxyl group in the case of GMA and hydroxylated backbones has been identified through mechanism-based research [30]. The evidence for the introduction of glycidyl methacrylate (GMA) or acrylating agents into castor oil-derived substrate materials is based on FT-IR and ^{1}H-NMR spectroscopy data which indicate that the intensity of the hydroxyl (–OH) band has decreased (i.e., there is less –OH present); the disappearance of the –OH peak suggests that all available –OH groups have been consumed during the grafting process; the bands associated with the –OH group are typically found around 3500 cm^{-1}; and this decrease is matched by an increase in intensity of peaks attributable to the acrylate or methacrylate double bonds as evidenced by the infrared spectra of the reacted materials.

2. Route 2- Pre-Functionalization of Cyclic-Carbonate Monomers

Acrylate is added during pre-functionalization prior to NIPU formation. Both carbonate and vinyl functional groups have been incorporated into the acrylated cyclic carbonates; examples include glycerol carbonate methacrylate (GCMA) or glycidyl carbonate acrylate (GCA). Villa *et al*. described an environmentally friendly route to the chemo-enzymatic conversion of glycidol and CO2 to produce ionic liquid-based dual-reactive monomers for the single-step formation of PHUs. The method eliminates a distinct acrylation step and thus reduces the amount of solvent required and produces architectures compatible with Stereolithography/Digital Light Processing (SLA/DLP) printing resins [31]. However, acrylated cyclic carbonates can require inhibitors e.g., Monomethyl Ether Hydroquinone(MEHQ) in storage to inhibit premature polymerization. Schimpf *et al*. and Buchheit *et al*. found that the distribution of acrylate in the structure of the material (i.e., chain end vs. side group) is controllable, and therefore both the gel fraction and the mechanical response of the material can be controlled. For example, they demonstrated that controlling the concentration of acrylate used will determine the cross-link density of the resulting PHU, and therefore affect the physical/mechanical properties of the material (tensile strength and modulus) [26].

3. Route 3 – Hybrid and Addition-Based Strategies for NIPUA Synthesis

The application of hybrid, and addition-based synthetic strategies has become an increasingly important way to develop non-isocyanate polyurethane acrylates (NIPUA), since these approaches provide the ability to carry out more than one chemical reaction at the same time to address the inherent deficiencies of traditional non-isocyanate polyurethane (NIPU) synthetic methods. Conventional NIPU systems are typically limited by their slow curing rates, the need for elevated temperatures during processing, and limited control over the architectural structure of the cured polymer network [25]. The integration of urethane chemistry into the acrylate-based reactions of polycondensation, Michael-type addition, and emulsion polymerisation enhances the processability of NIPUA systems, improves their curing rates, and provides materials with better performance characteristics [12, 25]. Hybrid and multifunctional approaches to creating new non-isocyanate polyurethane materials enable the incorporation of multiple functional groups (such as epoxy, acrylate, vinyl, siloxane), and different types of macromolecules (for example, copolymers, side-chain functionalities, hybrid networks) within the polymer backbone [12]. In addition, selection of specific monomers and the design of hybridization routes allow researchers to alter cross-link densities, polarities, mechanical properties, hydrophobicity, etc., for a variety of desired application-specific end-uses [9].

3.1 Polycondensation via Transurethane Chemistry

Transurethane Polycondensation is a hybrid process to create polyurethane polymers using non-isocyanate precursors. Dicarbamates react with diols through an exchange reaction. Urethane linkages are formed and low molecular weight alcohols are released as byproducts [21]. The chemical mechanism for this polymerization is analogous to conventional polyurethane, but it does not involve isocyanates as intermediates [21]. Boisaubert *et al*. were among the first to illustrate the applicability of transurethane polycondensation for generating polyurethane oligomers which may be functionalized after generation. They illustrated that both alkyl and aromatic dicarbamates react rapidly with diols under elevated temperature conditions (140 – 180 °C) to generate well-defined polyurethane backbones. Further, they showed that when hydroxyl-functional acrylates or acrylate-terminated diols were incorporated into the polycondensation process, urethane oligomers containing acrylate functional groups at each terminus could be generated in one-step. Since then, numerous other investigations have been completed to expand this process to the preparation of non-isocyanate polyurethane acrylates. Pascault and colleagues demonstrated that transurethane oligomers generated from acrylate functionalities exhibit excellent UV-reactivity resulting in highly cross-linked networks through photopolymerization [32].

3.2 Aza-Michael Addition and Diacrylate-Based Network Formation

The Aza-Michael addition reaction is a growing area of research as it presents a mild, yet efficient, hybrid route to synthesize NIPUA's. This nucleophile addition reaction occurs when amines react with electron-deficient vinyl groups, such as acrylates, at room temperature or slightly above, and produce beta-amino ester linkage bonds. Most reactions are conducted without any type of catalyst and are highly selective, capable of reacting with a variety of functional groups [12]. Zhang *et al*. have shown a single-step method to create NIPUA networks using the Aza-Michael addition of diamines with diacrylates. They have also shown that multifunctional amines will quickly react with diacrylate monomers to produce cross-linked polymer networks without needing UV light or thermal curing [32]. Of the approximately 85% of the network connections due to benzene-dicarboxylate-derived linkages indicate a high degree of conversion and effectively connect the network together. Liu *et al*. have found similar results while investigating additive-manufactured aza-Michael-based non-isocyanate polyurethane systems. The authors have shown that aza-Michael addition combined with residual acrylate polymerization can be used to precisely control cross-linking density and make the material suitable for 3D

printing and rapid prototyping. Zou *et al*. have examined the application of multifunctional bio-based diamines in aza-Michael NIPUA systems [44].

3.3 Emulsion Polymerization and Waterborne Hybrid Strategies

Waterborne hybrid strategies combining non-isocyanate polyurethane chemistry with acrylic emulsion polymerization for lower environmental impact reduced VOC emissions and potentially lower environmental impact NIPUA coatings.

The development of waterborne hybrid coating technologies combining non-isocyanate polyurethane chemistry with acrylic emulsion polymerization has been motivated largely by regulatory constraints limiting the use of solvent-based coatings; and by an increasingly greater demand for sustainable coating materials [26]. Fei *et al*. have utilized cationic polymerizable macro-surfactants for the preparation of polyurethane-acrylate nano-emulsions. Their research demonstrated that polyurethane chains containing both acrylate and ionic functionalities can serve as both the reactive component(s) and emulsifier for such systems. The resultant nano-emulsions displayed mean diameters <100 nm, stable colloids and low VOC content. The majority of the systems described were prepared utilizing isocyanates as the polyurethane precursor. However, it was also shown that the same methods may be used to prepare NIPUA systems using acrylated NIPU macromonomers prepared via cyclic carbonate –amine chemistry. In their study, Zhou *et al*. demonstrated that polyurethane–acrylic hybrid emulsions exhibit improved film formation characteristics and enhanced corrosion resistance when compared to traditional acrylic latices. This improvement in barrier performance and mechanical properties is directly attributed to the nanoscale structure developed during the emulsion polymerization process. In addition, the incorporation of reactive emulsifiers and bio-based polyols in the formulation of waterborne NIPUA systems has been shown to provide significant improvements in adhesion and flexibility on metal substrates [37].

4. Structure Property Correlations.

The type of reaction used for the acrylation is the determining factor for the structure and function of the polymer network, as well as its performance. Generally speaking, esterification is a means of producing high-density networks in film form with high rates of cure (i.e., fast), and also increases film hardness. While it is true that too much cross-link density can limit the flexibility of coatings by restricting polymer chain movement, this has been reported as being less than the loss of flexibility from using too many functional groups [30] . The GMA-grafted system provides the polymer network with free hydroxyls on the polymer backbone, thus increasing both adhesion and impact strength by enhancing the degree of interaction between molecules, as well as providing a higher degree of cross-linking. Too much methacrylate functionality in the GMA-grafted system will cause an increase in brittleness by limiting the movement of segments in the molecular structure. Pre-functionalization of the cyclic-carbonate system allows for a more even distribution of the acrylate functionality throughout the polymer network. The pre-functionalization process will allow for better homogeneity of the polymer network and better control over elastic modulus, and therefore, the performance characteristics of the coating. Additionally, the use of pre-functionalized monomers requires additional processing steps in order to synthesize them, and may add to the overall complexity of the manufacturing process [4].

Aza-Michael addition and transurethane polycondensation are two one-step approaches to produce non-isocyanate polyurethanes at relatively low temperatures, with minimal amounts of catalyst needed. These approaches have a lower processing complexity compared to conventional acrylation techniques. Therefore, they have a greater potential for scalable commercial applications. However, Aza-Michael addition and transurethane polycondensation processes are typically characterized by slow reaction kinetics and incomplete conversions, which can be limitations in their ability to be implemented commercially [12].

Table 2: Critical Comparison of Major Synthesis Strategies for Bio-Based NIPUA Systems: Mechanistic Features, Advantages, and Limitations

Synthesis Strategy	Mechanistic Characteristics	Major Advantages	Key Limitations / Durability Concerns	Industrial Scalability	References
Direct acrylation of NIPU prepolymers	Acrylate groups introduced through esterification of hydroxyl-functional NIPU chains	High crosslink density, rapid UV curing, improved hardness and chemical resistance	Excessive crosslinking may reduce flexibility and increase brittleness; incomplete acrylate conversion is possible	Moderate; multistep synthesis and viscosity increase may complicate processing	[30,28]
Glycidyl methacrylate (GMA) grafting	GMA reacts with hydroxyl or carboxyl groups, introducing methacrylate functionality	Improved adhesion, impact resistance, and tunable curing behaviour	High methacrylate content may restrict chain mobility and increase shrinkage stress	Good industrial feasibility because of commercially available monomers	[31]
Pre-functionalized cyclic carbonate monomers	Cyclic carbonate monomers are synthesised with built-in acrylate functionality before aminolysis	Uniform acrylate distribution, improved network homogeneity, controlled architecture	Additional monomer synthesis steps increase production complexity and cost	Moderate scalability depending on monomer synthesis efficiency	[31]
Aza-Michael addition approach	Sequential amine–acrylate addition followed by secondary crosslinking reactions	Catalyst-free or low-catalyst synthesis under mild conditions; greener processing	Slower reaction kinetics and incomplete conversion may affect final mechanical performance	High potential because of simplified one-pot processing	[29]
Transurethane	Dynamic exchange reactions	Reduced isocyanate	Elevated reaction	Promising but still	[24,]

polycondensation	generate urethane-acrylate hybrid structures	usage, adaptable network formation, improved sustainability	temperatures and viscosity control remain challenging	under development for large-scale production	
Waterborne NIPUA nanoemulsions	Hybrid polyurethane–acrylate particles dispersed in aqueous medium	Low VOC emissions, environmentally friendly processing, and safer industrial applications	Water sensitivity, storage stability, and slower drying rates remain concerns	Strong industrial relevance for sustainable coatings	[18, 37]
UV-curable NIPUA systems	Radical photopolymerization of acrylate-functional hydroxyurethane oligomers	Fast curing, low-energy processing, high hardness and gloss	Oxygen inhibition and incomplete double-bond conversion may reduce long-term durability	Highly suitable for coatings, printing, and electronics industries	19, 23]
Dynamic covalent NIPUA networks (imine, Diels–Alder, boronic ester)	Reversible covalent bond exchange enables adaptive network rearrangement	Self-healing, recyclability, stress relaxation, reprocessability	Hydrolytic instability or thermal sensitivity may limit environmental durability	Emerging smart-coating technology with growing industrial interest	[11, 17, 28]

The performance of bio-based NIPA systems depends greatly upon the network structure (Table 2), acrylate distribution, and cross-linking mechanisms. The direct acylation and UVA-curable techniques generally yield better hardness and curing efficiencies due to faster photo-polymerization rates and greater cross-link densities. However, the extreme rigidity of these networks can be detrimental to their ultimate flexural properties and crack resistance over time. Aza-Michael and dynamic covalent techniques are more environmentally friendly and have the potential for self-healing characteristics; however, they suffer from slow kinetic reactions and environmentally sensitive reactions. While waterborne (NIPUA) nano-emulsions may be able to decrease VOC emissions and offer both regulatory and process-related benefits over solvent rich formulations.

Synthesis Strategies and Developments in Non-Isocyanate Polyurethane-Acrylate (NIPUA) Systems

The advances in the last few years in Non-Isocyanate Polyurethane-Acrylate (NIPUA) chemistry have focused on developing a new generation of coatings and photocurable products with high performance and low environmental impact using 2-Hydroxyurethane functionalities associated with Acrylate functionalities. The introduction of Acrylate functionalities into the NIPU backbone allows for rapid curing under UV radiation, excellent mechanical and surface properties, In addition to offering a non-isocyanate route to formulating polyurethanes, the performance and environmental characteristics of resultant materials also have a strong dependence on the chemical structure of precursors, the overall architecture of polymer networks; processing conditions for forming the material; and final formulation compositions [62, 84]. Most commonly, the preparation of NIPUs is achieved through the ring-opening polyaddition of cyclic carbonates (propylene carbonate or glycerol carbonate) with diamines to generate 2-hydroxyurethane-polymers [29]. These polymers are subsequently acrylated with (meth)acryloyl chloride or glycidyl methacrylate to provide reactive double bonds, forming NIPUA oligomers capable of being cured upon UV or LED exposure. Additionally, the development of glycerol carbonate (meth)acrylate (GCMA) and glycerol carbonate acrylate (GCA) monomers, which utilize CO2 and glycidol as starting materials, has enabled "green" syntheses of NIPUA. A sustainable chemo-enzymatic method to produce GCMA with ionic-liquid catalysis was recently demonstrated by Villa *et al*. [31], while Morales-Cerrada *et al*. showed that GCMA is an effective cross-linker in hydroxyurethane-acrylate networks and enhances both adhesion and coating toughness. The more recent developments have extended the range of NIPUA chemistry beyond coatings to include additive manufacturing and biomedical applications [31]. Photosensitive NIPUA resins were prepared by Wang *et al*. in two-steps: the opening of propylene carbonate with isophorone diamine occurred in the first step; after which the resin was methacrylated and then Poly(ethylene glycol) diacrylate (PEGDA) was added. The resulting resin possessed significantly improved tensile (63.9 MPa) and flexural (90.8 MPa) strength, excellent thermal stability (T50 = 254°C), and excellent biocompatibility with bone (MC3T3-E1) and muscle (C2C12) cells. Compared to commercially available photoresins, a neutral or minimal inflammatory response *in vivo* during implantation was demonstrated, which evidenced their medical-grade safety [21].

Conclusion and Future Perspectives

Bio-based non-isocyanate polyurethane-acrylates represent a relatively new area for study within the fields of polymer and coatings science as they have the potential to offer isocyanate alternatives from renewable resources while also using fast acrylate based curing processes. Although recent reported systems have shown good curing performance, hardness, adhesion, chemical resistance, gloss etc., these physical and mechanical properties are highly dependent upon many factors including the type of precursor materials used, the number of reactive groups per molecule (acrylate functionality), degree of cross-linking achieved through curing reaction, curing conditions and composition of the formulated system [7, 18, 24]. As this review will show, the synthesis approach is very influential on the overall architecture, durability and performance characteristics of NIPUA coatings. There are a number of different synthetic methods that can be employed when producing these coatings, which include direct acylation, functionalized cyclic carbonate monomers prior to reaction with acrylic functionalities, aza-Michael additions, transurethane polycondensations, and water-borne hybrids. Each method produces coatings with unique curing behaviour, cross-linking densities, flexibilities and stabilities over time. While there have been numerous reports on how increased acrylate functionality and network cross-link density in reported systems influence coating properties (i.e., increased hardness and chemical resistance) — too much cross-linking has shown to result in reduced molecular mobility, crack

resistance, as well as decreased coating flexibility. Hence, the relationship between acrylate functionality and coating performance is both dependent upon the formulation of the system as well as the resulting network structure.

A few of the major challenges facing the conversion of reported lab-scale bio-based NIPUA systems into commercially acceptable products include: achieving longer term durability, establishing a balance of structural-property relationships, developing scalable methods for synthesizing the materials, and demonstrating cost-effectiveness. While all of these represent significant hurdles for commercialization, it is clear that durability is currently the most pressing challenge due to insufficient evaluation of hydrolytic degradation, UV aging, thermal oxidation, abrasion, corrosion, and adhesion loss. Therefore, the primary focus of future research efforts should be directed toward standardizing durability tests and validating their results through field trials, while simultaneously addressing issues associated with controlling cross-link density, acrylate functionality, hydrogen bonding, and dynamic bonds to establish a balance between mechanical hardness, flexibility, toughness, and self-healing behavior. An additional area of focus from a commercial standpoint should be the development of strategies to decrease the costs associated with precursor materials, improve reaction kinetics, better control viscosities during the polymerization process, scale up multi-functional cyclic carbonate and acrylate syntheses, and develop low-energy consuming water-borne and UV curable processes.

List of Abbreviations

PU:Polyurethane, NIPU:Non-Isocyanate Polyurethane, NIPUA:Non-Isocyanate Polyurethane Acrylate, PHU: Poly(hydroxyurethane), CC: Cyclic Carbonate, VOC:Volatile Organic Compound, UV:Ultraviolet, HEMA: 2-Hydroxyethyl Methacrylate, IPDA:Isophorone Diamine, EDA:Ethylenediamine, HMDA:Hexamethylene Diamine, MEHQ:Monomethyl Ether Hydroquinone, MAAH:Methacrylic anhydride, FTIR:Fourier Transform Infrared Spectroscopy, NMR:Nuclear Magnetic Resonance, DSC:Differential Scanning Calorimetry, TGA:Thermogravimetric Analysis, SEM:Scanning Electron Microscopy, TEM: Transmission Electron Microscopy

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