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Bio-based non-isocyanate polyurethanes: Recent progress toward self-healing and sustainable polymer materials

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Abstract
The transition from conventional polyurethane (polyurethane) to non-isocyanate polyurethane (non-isocyanate polyurethane) is largely influenced by increasing concerns about safety, environment and sustainability associated with the classical PU technology. Non-isocyanate polyurethane is a promising alternative since they can overcome some of the problems of conventional PU manufacture, in particular the use of dangerous isocyanates and the phosgenation process. Recently there was a lot of interest in the field of bio-based non-isocyanate polyurethanes as part of the concepts of green chemistry and sustainable materials engineering. Vegetable oils have become increasingly popular as a source for NIPU due to its availability, renewability, biodegradability, low toxicity and lower price compared to other alternatives. This review therefore aims at providing an overall view of vegetable oil based NIPUs and their developments in recent times. This paper will be dealing with the syntheses methods and ecologically favorable methods used in the production of NIPU's. Special focus will be placed on the polyaddition-reaction between cyclic carbonates and amines that is considered to be one of the most promising routes to sustainable NIPU-syntheses. Furthermore the synthesis-routes, starting-materials, cyclic-carbonate-chemistry and amine-curing-agents will be described. Additionally, the physical/chemical properties and application possibilities of NIPUs derived from vegetable oils such as e.g. soybean-oil, linseed-oil, sunflower-oil etc., i.e. heat resistance, mechanical properties, self-healing and recyclability will be highlighted. Finally the review shall discuss the industrial applicability, market-potential, actual hurdles and future prospects of the NIPU-technology.

Keywords: Bio-based non-isocyanate polyurethane, NIPU, Polyhydroxyurethane, Self-healing polymers, Dynamic covalent chemistry, Cyclic carbonates, Vegetable oils, Sustainable coatings, Vitrimers, Renewable polymers.

Introduction

Polyurethane (PU) represents one of the most widely used polymeric materials today due to their remarkable mechanical and physical properties. From the first reports of Otto Bayer's invention of PU in the early 1930s onward, polyurethanes have become ubiquitous across a range of industries; including coatings, foams, adhesives, elastomers, medical devices, textile products, vehicle components, and building materials [1]. As a result, there is continually increasing worldwide demand for polyurethane based upon the variety of possible applications combined with its inherent tunability in terms of physico-chemical properties [2]. Although conventional polyurethane materials exhibit many beneficial properties, the manufacturing process presents numerous environmental and health risks. For example, traditional PU manufacturing processes involve the use of hazardous chemicals, such as toxic isocyanates and phosgene derived intermediate compounds. Isocyanate exposure can lead to respiratory disease, skin irritation and even occupational asthma. Phosgene is considered an extremely dangerous industrial chemical [3]. Non-isocyanate polyurethane (NIPU) has emerged as a viable alternative method for producing environmentally acceptable polyurethane systems since they do not utilize toxic isocyanates throughout their synthesis process. Typically NIPU systems are manufactured using the reaction of cyclic carbonates with amines. The resultant product will be a polyhydroxy urethane structure without producing any undesirable byproducts [4]. The aforementioned synthetic pathway exhibits many benefits including reduced toxicity, decreased VOC emissions during curing, better working conditions for workers, higher atom economy and environmentally favorable manufacturing conditions.

Thus this review provides a comprehensive update concerning vegetable oil-based self-healing non-isocyanate polyurethane systems with special attention given to eco-friendly synthesis pathways/cyclic carbonate chemistry/non-petroleum based feedstocks/self-healing mechanisms/recyclability/reprocessability/multifunctional application areas. Furthermore, this review will critically examine the correlation between molecular design/dynamic covalent chemistry/healing performance while highlighting present research challenges and future possibilities for developing new generations of smart and sustainable NIPU materials.

Insight into PU and NIPU

Polyurethane (PU), as a large family of polymers that have a backbone linkage that contains the urethane group resulting from reaction between an isocyanate compound with a hydroxyl group containing compound [5]. As typically, PU will contain alternating "hard" and "soft" segments. The isocyanate portion of the polyurethane will be part of the hard segment; the polyol portion will be part of the soft or flexible segment of the polymer matrix [6]. The relative amounts of hard and soft segments within the structure of a polyurethane play a major role in establishing many of its physical, thermal, mechanical, and chemical properties.

Generally, when there is a larger amount of isocyanate in a given polyurethane than polyol, the polyurethane tends to form a harder and more hydrophobic structure. When there is a greater amount of polyol in a polyurethane than isocyanate, the polyurethane forms a softer and generally more hydrophilic material [7]. Because the polyurethane structure is greatly influenced by the relative ratios of polyol to isocyanate used in making it, precise control over this ratio may be necessary to obtain desirable physical and chemical characteristics for use in particular applications. Many types of additives are commonly added to the mixture of reactants to enhance the processing characteristics of the resultant polyurethane. Some examples of additives used in forming polyurethanes include catalysts, surfactants, blowing agents, plasticizers, pigments, chain extenders, fillers, flame retardants, smoke suppressants, and stabilizers [8].

The properties of polyurethane materials range from rigid/brittle to highly flexible/elastic, based upon the selection of polyols and isocyanates. The isocyanates that react with polyols contain a very reactive group called an isocyanate group (R—N=C=O), and come in both liquid and solid form for commercial applications [8]. Isocyanates can also be divided into categories based on the chemical structure of the R group; these include aliphatic, cycloaliphatic, aromatic, and polycyclic types. Aliphatic isocyanates tend to have lower reactivities due to less resonance stabilization of the negative charge. Because of this reason, diisocyanates that contain two isocyanate functional groups are the most commonly used type [5].

Production route of NIPU

The development of NIPUs has also followed from increasing interest in environmental protection and green chemistry. The strict controls imposed on VOC emissions and the health risks associated with isocyanate exposure are other factors that have driven efforts to find alternatives to traditional polyurethane. There have been several recent reviews of the synthesis of NIPUs, which provide a detailed overview of all of the different synthetic routes and highlight the rapid developments occurring within this area.

1. Polycondensation

Polymer condensation is a classical chemical method used for a long time for the synthesis of nonisocyanate polyurethanes (NIPUs). Polymer condensation uses various combinations of precursors in the form of polychloroformates and polyamines, polycarbamates and polyols, polycarbamoyl chlorides and polyols, polycarbonates and polyamines. Although there are many different ways to synthesize polymers using polymer condensation, they do not appear to be very industrially relevant due to several technical and environmental issues [9]. There are two main technical/chemical problems associated with the polycondensation reaction route. Firstly, all the polycondensation routes require either phosgene or derivatives of phosgenoligomers. These compounds pose serious health risks; therefore, handling them is hazardous. Secondly, most polymer condensation reactions produce byproducts in the form of HCl and alcohols that need to be separated from the desired product in order to obtain a pure material. Separation of the by-products increases the difficulty and cost of the process. More recently researchers have made efforts to address these technical/chemical issues using greener methods. For example, Wołosz *et al*. proposed an alternative green chemistry based method that utilizes dimethyl carbonate (DMC), an environmentally friendly compound, as a substitute for phosgene and diamines for synthesizing alkylene and arylene bis(methyl carbamate)s [10].

2. Rearrangement

Rearrangements are an additional method to produce Non Isocyanate Polyurethanes (NIPUs) through Synthetic Methods. The rearrangement mechanism typically uses Acyl Azides, Carboxamides and Hydroxamic Acid Derivatives to produce reactive intermediate species from rearrangement reactions. The three main types of rearrangements include Curtius, Hofmann, and Lossen rearrangements. Rearrangements have drawn considerable interest in recent years due to their ability to create polyurethane polymers using isocyanates as intermediates. The development of Continuous Flow Microreactor Technologies has contributed to the increase of practicality associated with rearrangement based NIPU synthesis. Continuous flow reactor technology increases the rate at which chemical reactions occur, allowing the reduction in time required for the reaction to reach completion. Additionally, the reactor system provides a safer environment than traditional batch reactors by containing and controlling the highly reactive azide intermediates involved in these reactions. In a related study, Mallia *et al*. demonstrated that kilogram quantities of polycarbonate diols could be produced through a continuous flow Curtius rearrangement [11].

3. Ring-Opening Polymerization

The use of ring-opening polymerization (ROP) is a very important means for the preparation of non-isocyanate polyurethanes (NIPUs). The majority of these processes involve the polymerization of aliphatic cyclic carbamates or aziridine-based monomers via ring-opening reactions [12]. The primary advantage of this process is that no low molecular weight products are generated during polymerization; therefore, purification procedures are simplified and an improved atom economy is achieved.

Although there are many advantages associated with using ROP for the preparation of NIPUs, there are several limitations. One major issue has been the fact that most cyclic carbamate precursor monomers used today are synthesized from phosgenated chloroformates. Therefore, even though this synthetic route eliminates the problems of toxic byproducts and environmentally unfriendly aspects associated with traditional polyurethane chemistries, many of the problems still remain. When aziridines are used as monomers, they present additional hazards due to their high toxicity and sensitization potential [13].

4. Polyaddition

NIPU polyaddition chemistry that utilizes cyclic carbonates (CCs) and amines is gaining momentum due to inherent advantages over prior methods. The use of amines in place of toxic isocyanate and phosgenated intermediate reduces the potential for exposure to harmful chemicals during synthesis. As a result, this method of forming NIPUs produces less waste, provides for safer working conditions and supports a more eco-friendly environment; all of which are important factors when producing polymers using sustainable processes. A study conducted by Cornille *et al*. was published in 2015 reporting on the use of cyclic

carbonates reacting with diamines to produce rigid and flexible high density NIPU foams (194-295 kg/m^3). These produced foams had excellent thermal stability and were able to recover well under compressive forces. When amines react with cyclic carbonates via polyaddition, it involves an attack by the nucleophilic amine onto the electrophilic carbonyl carbon found in the cyclic carbonate ring. This carbon is located either in a five-membered or six-membered ring structure. Following the proton transfer reaction, the ring opens, creating new urethane bonds with hydroxyl functionalities. Because these hydroxyl groups become a part of the polymer chain, the material created after curing is typically called polyhydroxyurethane (PHU). Hydroxyl functionality creates extensive hydrogen bonding throughout the polymer structure. Therefore, PHU's have better chemical resistance to non-polar solvents than other polymers. Additionally, a wide variety of cyclic carbonates and amines derived from renewable biomass, biodegradable, and sustainable resources can be used as precursors to create a large number of different PHU formulations [14].

Cyclic Carbonates for NIPU Synthesis

Cyclic Carbonates (CC's), along with many other intermediate compounds, represent one of the major precursors to the formation of non-isocyanate polyurethanes (NIPU's). While their growing popularity is largely attributable to the fact that they can polymerize with amines via polyaddition reactions at ambient temperatures without using potentially hazardous isocyanates and/or phosgene derived compounds as intermediates, cyclic carbonates offer an additional advantage; namely, a safe route to produce these polymers. In terms of versatility, cyclic carbonates may also be produced from either petrochemical based and renewable sources. Additionally, the development of cyclic carbonate chemistry is attracting considerable interest due to its potential application to utilize carbon dioxide and integrate renewable resources into the production process. As previously noted, the chemical reactivity of cyclic carbonates is dependent upon several factors including the size of the ring system, electronic effects associated with substituents attached to the ring, steric hindrances caused by bulky substituents and the degree of electron withdrawal by those substituents. As described in detail elsewhere in this dissertation, during aminolysis reactions cyclic carbonates will undergo nucleophilic ring opening by amines producing urethane linkages and hydroxyl functional groups. This results in increased inter-molecular hydrogen bond interactions in polyhydroxyurethane (PHU) networks leading to improved physical properties such as adhesion, tensile strength, thermal stability and chemical resistance [15].

1. Classification of Cyclic Carbonates

Cyclic Carbonates are normally categorized by ring size into Five-Membered Cyclic Carbonate (CC-5) Six-Membered Cyclic Carbonate (CC-6) and Higher Membered Cyclic Carbonates. The most studied group of Cyclic Carbonates is Five-Membered Cyclic Carbonates. This is primarily based upon the relative simplicity of synthesis, commercial availability, and compatibility with bio-based feedstocks [16]. These cyclic carbonates can be produced via the reaction of CO2 with an epoxide to produce a cyclic carbonate that exhibits good chemical stability. Nonetheless, systems composed of five-membered cyclic carbonates typically demonstrate lower reactivity towards amines as a consequence of reduced ring strain energy. The reactivity of six-membered cyclic carbonates is higher than that exhibited by five-membered cyclic carbonates owing to increased ring strain, and favorable ring opening thermodynamic conditions [17]. Consequently, CC6 systems often result in faster aminolytic reactions and greater polymerization efficiencies. Nonetheless, the synthesis of CC6 systems is normally more complicated, and may require toxic reactants or multi-step processes; consequently limiting broader industrial use.

2. Synthesis of Cyclic Carbonates

A number of synthetic routes exist for the preparation of cyclic carbonates. The largest volume method currently in practice, the epoxide-carbonate route involves the conversion of unsaturated substrates (such as vegetable oils) into functionalized intermediates through an initial epoxide forming step; these functionalized intermediates are then reacted with CO_2 to give cyclic carbonates. In addition to being an efficient method for producing cyclic carbonates from plant derived materials; this method has the added advantage of utilizing CO_2 as a "renewable" C1 building block that can be used to make sustainable polymer precursors.

Due to its high atom economy and relatively small amount of by-products formed during the reaction, the carbonation of epoxides with CO2 represents a very eco-friendly method of synthesizing cyclic carbonates. A wide variety of homogeneous, heterogeneous, organometallic, ionic liquids and metal-free catalytic systems have been evaluated for enhancing the efficiency of carbonating epoxides at mild reaction temperatures. More recently, research has concentrated on finding catalyst-free and low energy methods for carrying out the carbonation reactions of epoxides to further increase the greenness of the overall process [18].

3. Bio-Based Sources for Cyclic Carbonates

Vegetable oils have been extensively researched as a renewable resource for cyclic carbonate synthesis due to their relative availability; biodegradability; lower toxicity than fossil fuels; and the variability in structure that they exhibit. Bio-epoxides synthesized from soybean oil, linseed oil, castor oil, sunflower oil and canola oil are typically converted to cyclic carbonates which can be used as reactants in NIPU production. Vegetable oils also contain triglyceride structures with naturally occurring unsaturated double bonds which provide an ideal target for chemical modification.

Overall, cyclic carbonate chemistry plays a critical role in the development of sustainable NIPU materials. The combination of renewable feedstocks, carbon dioxide utilization, and tunable polymer properties makes cyclic carbonates highly attractive intermediates for the fabrication of environmentally friendly and multifunctional polyurethane systems. Although vegetable oil-derived cyclic carbonates are widely used for NIPU synthesis, significant differences exist in functionality, reactivity, and final polymer performance. Most studies focus on soybean and linseed oils, whereas comparatively little attention has been given to lignin-, vanillin-, and cardanol-derived cyclic carbonates. Furthermore, scalability and cost analyses remain largely unexplored, limiting industrial implementation.

Self-Healing Non-Isocyanate Polyurethane (NIPU)

Self-healing Non-Isocyanate Polyurethanes (NIPUs), a new generation of environmentally friendly self-healing polyurethanes, utilize non-toxic isocyanates and dynamic covalent bonds instead of traditional isocyanates. Most of the early NIPU research identified their potential as viable alternatives to conventional self-healing polyurethanes; however, they suffered from lower mechanical performance and reduced ability to heal efficiently at room temperature. In an effort to improve upon earlier methods for creating NIPUs. One of the greatest improvements in self-healing NIPUs has been the incorporation of dynamic chemical reactions into their backbones, including reversible urethane linkages, hydrogen-bonding networks, and controlled movement of the soft segments. In their research on NIPU systems with increased structural integrity and adaptable functionality, Gholami and Yeganeh identified two significant factors influencing the healing performance of NIPUs: the degree of segmental mobility and the degree of cross-linking density. unfortunately, they also identified that higher degrees of cross-linking densities increase mechanical strength but severely limit chain mobility and therefore reduce healing efficiency.

Table 1: Mechanical Properties of Bio-Based NIPU Films

NIPU System	Tensile Strength (MPa)	Elongation at Break (%)
Soybean oil NIPU film	0.35–1.35	2.2–4.5
Soybean oil NIPU membranes	1.7–6.2	165–306
Soybean oil NIPU film	0.3–11.1	3–433
Soybean oil NIPU film	1.8–6.2	152–309
Canola oil NIPU film	5–8	103–192
Jatropha oil NIPU film	4–17	30–230
Linseed oil NIPU film	2–18	1–310
Soybean oil NIPU film	7.2–10.1	80–97
Sunflower oil NIPU film	0.9–5.2	100–240
Linseed oil NIPU film	11.9–18.9	26.0–57.1
Linseed oil NIPU film	5.0–9.5	214.8–327.3
Soybean oil NIPU film	0.45–0.97	36.7–92.0

Bio-based polyols and cyclic carbonates have greatly impacted NIPU chemistry in terms of synthesis. The use of renewable resources to replace petroleum based feedstock for NIPUs was demonstrated by Javni *et al*. to maintain satisfactory levels of polymer performance [19], although, few studies report intrinsic dynamic bond exchange within bio-based NIPUs; thus, all reports indicate self-healing must be achieved via some form of additional functionalization as opposed to being a native property of the polymer backbone.

Conversely, soybean-oil based NIPU formulations show an enormous breadth of mechanical characteristics (0.3 – 11.1 MPa tensile strength and 2.2 – 433% elongation). The variations observed here indicate the strong formulation dependent nature of soybean derived NIPUs. Wherein small variations in curing parameters, composition of the soft segments, and degree of cross-linking can produce dramatically different end-use mechanical behaviors. In addition, while there are examples of formulations of extreme flexibility (up to 433% elongation) these are most commonly associated with lower tensile strengths, thereby confirming the well-known trade-off inherent to simultaneously optimizing elastic behavior and mechanical reinforcement. The bio-based NIPU films' strength—stretching performance diagram visually represents the relationship between mechanical stiffness and toughness from varying bio-based materials (feedstocks) to each other. Most of the NIPU's exhibit an identifiable diagonal trend that indicates the majority of these materials follow the same pattern of decreasing tensile strength with increasing elongation at failure for most cross-linked polymer networks. The linseed oil based NIPU is located on the right side of the high-strength-low stretch area because it has the highest amount of cross-linkage and therefore the stiffest structure. On the other hand, the soybean and sunflower oil based systems have a large range of values for both low tensile strength and high elongations, indicating they possess a high degree of molecular movement and decreased density of their polymer network.

Dynamic Self-Healing Mechanisms in Bio-Based NIPUs

Self-healing properties in polymers allow damaged material to regain its structural integrity, mechanical function, and operational capabilities following a mechanical breakdown or fracture. The self-healing property in non-isocyanate polyurethanes (NIPUs) based upon biological materials is typically due to reversible dynamic interactions which permit repeated association/dissociation of bonds in response to external/internal stimuli. Reversible interaction allows damaged polymer networks to reassemble, reconnect, and heal following mechanical injury, thus increasing the service life, durability and sustainability of these materials.

Bio-based dynamic self-healing NIPUs are primarily divided into two types of reversible mechanisms: reversible covalent dynamics and supramolecular interactions. Covalent dynamic systems consist of reversible chemical exchange reactions including imine exchange, disulfide metathesis, boronic ester exchange, Diels-Alder cycloaddition, and transcarbamoylation reactions. This type of reversible covalent connection produces relatively stable adaptable polymer networks that can repeatedly heal and recycle while preserving structural integrity. Supramolecular systems, on the other hand, utilize non-covalent reversible interactions including hydrogen bonding, ionic interactions, π-π stacking, host-guest interactions, and metal-ligand coordination. Of all the strategies available for developing self-healing NIPUs, dynamic covalent chemistry has become particularly prominent because it enables the combination of structural robustness with reversible adaptability of the polymer network. Bio-based NIPUs are increasingly being developed using multifunctional dynamic chemistries capable of providing simultaneous self-healing properties, recyclable/reprocessable properties, shape memory effects and environmentally friendly performance characteristics [20].

Structure–Property–Healing Relationship in Bio-Based Self-Healing NIPUs

The performance of self-healing biodegradable (bio-based) non-isocyanate polyurethane (NIPU) polymers depends on the relationship among molecular composition, polymer network topology, and time-dependent interchange of dynamic covalent bonds. In addition to determining the thermal and mechanical characteristics of the polymer network, the chemical composition dictates the rate,

frequency, and effectiveness of the self-healing process. Thus, it is necessary to understand the relationships among structure, property, and healing in order to design multifunctional NIPUs that can be used to create materials having both high mechanical properties and the ability to autonomously repair damage. Cross-link density is one of the most significant structural variables that affects the healing behavior of self-healing NIPUs. A highly cross-linked polymer typically exhibits superior tensile strength, hardness, chemical resistance and thermal stability than a lightly cross-linked polymer because a highly cross-linked polymer has a denser covalently cross-linked network that restricts molecular movement and provides greater load transfer within the polymer matrix. On the other hand, over-cross-linking severely limits segmental mobility and diffusion of chains necessary for dynamic bonding exchange and crack closure during healing. Consequently, while a highly rigid self-healing NIPU system may have good mechanical properties, it will likely exhibit poor healing efficiency. Conversely, self-healing NIPU systems having low cross-link densities or being more elastic allow greater molecular rearrangements and interface diffusions resulting in faster and/or more efficient healing. Unfortunately, these less-rigid self-healing NIPU systems often lack sufficient mechanical strength and/or dimensional stability [21].

Industrial Challenges and Commercialization Barriers of Self-Healing Bio-Based NIPUs

One of the largest barriers to the use of self-healing bio-based non-isocyanate polyurethanes (NIPUs) in large scale industrial settings are numerous scientific, technological, economic, and processing issues. Laboratory-scale studies have shown promising results for self-healing characteristics, recycling, and environmental sustainability; however, it has proven difficult to translate laboratory-scale development of self-healing NIPUs into commercially viable products. Several self-healing NIPU systems reported in the literature still suffer from a number of limitations including mechanical durability, hydrolytic stability, healing conditions, scalability, and long term environmental performance. A very significant problem is the inherent trade off between mechanical durability and healing efficiency. To be able to heal effectively, there needs to be sufficient chain mobility in order to facilitate molecular diffusion and dynamic bonding exchange at damaged interfaces [22]. Ultimately, despite having vast potential as sustainable coatings/adhesives/elastomers/smart-materials, there are numerous unaddressed scientific and engineering challenges associated with self-healing bio-based NIPUs. Therefore, success in commercializing self-healing bio-based NIPUs will likely hinge on the ability to establish acceptable balances among mechanical property durability/healing performance/processability/cost effectiveness and environmental stability within scalable and industrially-compatible material systems.

Applications of Self-Healing Bio-Based NIPUs

Figure X describes the primary areas that self-healing bio-based non-isocyanate polyurethane (NIPU) will be used in as a result of its multi-functional use in future generations of engineered and biomedical systems. The diagram below illustrates five major industries that are targeted in terms of potential applications: protective/anti-corrosive coating formulations; wood adhesive formulations; flexible electronic devices and strain gauges; super-hydrophobic and smart coatings; and biomedical and soft materials.

1. Protective and Anti-Corrosion Coatings

Self-healing bio-based non-isocyanate polyurethane (NIPU)s have been gaining interest as potentially superior protective coating materials due to their use of renewable resources, lower toxicity than conventional coatings, ability to heal reversibly, and barrier properties against the environment. The primary limitation of traditional protective coatings is that micro-crack formation resulting from damage caused by abrasion, thermal shock, and/or environmental exposure provide an open pathway for oxygen, moisture, and corrosive ions to penetrate to underlying metal surfaces. Dynamic self-healing NIPUs can repair damaged areas via reversible chemical bonding exchange, thus preventing crack propagation and enhancing coating service life [23].

2. Wood Adhesives

The use of bio-based self-healing NIPUs is being increasingly considered as a sustainable option for wood adhesives. They exhibit several advantages over traditional (formaldehyde based) wood adhesives such as improved adhesive properties, recyclability, thermal resistance and lower environmental toxicity. A property of the hydroxyurethane network that enables the reversible reorganization of bonds upon damage is its ability to undergo dynamic covalent exchange reactions. This allows for the reconnection of mechanically damaged adhesive surfaces and partial restoration of adhesive strength [24].

3. Flexible Electronics and Strain Sensors

Flexible wearable strain sensor technology has become one of the most rapidly expanding application domains for self-healing bio-based NIPUs. These materials offer elastic properties combined with repeated deformation recovery and dynamic network restoration, which is unlike conventional electronic polymers. Self-healing NIPUs can recover both mechanical functionality and conductive paths after a material failure; therefore, they can improve the durability and life expectancy of devices by orders of magnitude [25].

4. Smart and Superhydrophobic Coatings

Smart, super-hydrophobic, self-healing, biobased non-ionic polyurethanes (bio-NIPUs) have been introduced as potential multi-functional materials. The use of smart and super-hydrophobic self-healing properties combined with self-cleaning, anti-fouling characteristics, and water repellent abilities, has made them very attractive and competitive multi-functionality material. In addition to their attractiveness, it is worth noting that this type of coating will be valuable for a variety of industries including automotive, marine, textile and electronics; where resistance to surface contaminants and/or water penetration is critical [26, 27].

5. Biomedical and Soft Materials

Biological and Soft-Material Applications of Self-Healing Bio-Based NIPUs may be a Promising Area of Development. The elimination of toxic isocyanate chemistry in self-healing soft-materials development will enable biologists to create adaptive biomaterials which can both flexibly respond to changes in their environment and

dynamically repair themselves. Recent advances in the construction of self-healing bio-compatible materials using renewable feedstocks such as lignin, vanillin, vegetable oil, and polysaccharides demonstrate significant promise in developing materials that could serve as wearable health monitoring systems, injectable medical devices, tissue engineering scaffolds, and flexible wearable bio-electronics [28].

Future Perspectives and Emerging Trends in Self-Healing Bio-Based NIPUs

The rising need for eco-friendly, smart and high-performance polymers has prompted significant advances in self-healing, bio-based, non-isocyanate polyurethane (NIPU) systems. In spite of these developments, current NIPUs continue to be limited by issues related to mechanical durability, the healing process, hydrolysis, the complexity of processing and manufacturing, and industrial scale-up. As a result, there is now a greater emphasis on creating multifunctional and adaptable polymer structures which can provide both sustainability and durable structure along with self-healing properties, recyclability, and environmental resistance [22].

One area that represents one of the most exciting new avenues of research in this field is developing hybrid multilayered polymer systems that include multiple dynamic interactions within a single material system. Single-dynamic systems based upon conventional systems often suffer from inherent drawbacks. For example, although imine bonds allow for fast healing, they lack good hydrolytic stability. On the other hand, Diels-Alder networks possess superior durability but only at elevated healing temperatures. By combining two or more different dynamic chemistries including imine exchange, disulfide metathesis, boronic acid/ester exchange, hydrogen bonding, and vitrimeric transcarbamoylation, researchers believe it is possible to create complementary effects that will enable the balance of healing kinetics and mechanical strength while providing enhanced environmental stability. It is anticipated that hybrid architectures will be essential to the creation of next-generation self-healing NIPUs [29].

Conclusion

Self-healing bio-based non-isocyanate polyurethanes (NIPUs) can be used to replace conventional polyurethane systems because they utilize less toxic chemicals, use renewable feedstocks, and allow for adaptive dynamic architecture. Since NIPUs contain dynamic reversible interaction through cyclic carbonate – amine reaction chemistry, it provides a base for creating sustainable environmentally friendly polymer systems that can perform self-healing functions, recyclable/reprocessable functions and longer service life functions. With these benefits self-healing bio-based NIPUs could become the next generation of intelligent coating/adhesive/elastomer/biomedical material/smart protective surface products.

The purpose of this review was to discuss the synthetic route to NIPU systems; types of biobased precursors available; fundamental chemistry involved in dynamic self-healing mechanisms; relationship between structure – property – healing; various applications of NIPU systems; current industrial challenges; and finally, future prospects for self-healing NIPU systems. The dynamic covalent chemistry approaches involving imine exchange, disulfide metathesis, boronic acid/ester exchange, Diels-Alder reactions, and vitrimeric transcarbamoylation were shown to effectively achieve reversible network properties and repeated healing behaviors. Similarly, supramolecular interactions using hydrogen bonding, ionic interactions, π–π stacking and metal-ligand coordination provide fast healing kinetic response under mild conditions. Despite all these advances there are a number of significant hurdles preventing the practical industrial realization of self-healing bio-based NIPUs. The main problem lies in the inherent trade off between mechanical toughness/healing efficacy. High cross-linked rigid polymer networks exhibit high tensile strength, thermal stability and chemical resistance but lack sufficient molecular mobility for effective healing. On the other hand, highly dynamic and flexible systems are good at healing capabilities but show low mechanical durability/dimensional stability. In summary, self-healing bio-based NIPUs represent an important advancement towards sustainable/multi-functionality based on the principles of Green Chemistry/Circular Economy. Although there are many scientific and industrial problems remaining unsolved related to self-healing NIPUs continued development in dynamic polymer chemistry/Renewable Feedstock Engineering/Intelligent Network Design will be required to accelerate the development of commercially viable self-healing NIPU systems. Future work should focus on scalable manufacture/ambient condition healing/long-term environmental stability/standardized performance assessment to bridge the gap between lab scale innovation/real world industrial application.

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List of Abbreviations

PU (Polyurethane), NIPU (Non-Isocyanate Polyurethane), PHU (Polyhydroxyurethane), CC (Cyclic Carbonate), CC5 (Five-Membered Cyclic Carbonate), CC6 (Six-Membered Cyclic Carbonate), VOC (Volatile Organic Compound), CO_2 (Carbon Dioxide), DMC (Dimethyl Carbonate), ROP (Ring-Opening Polymerization), DA (Diels–Alder), DCC (Dynamic Covalent Chemistry), DCAN (Dynamic Covalent Adaptive Network), DDCAN (Dual Dynamic Covalent Adaptive Network), Tg (Glass Transition Temperature), GO (Graphene Oxide), CNC (Cellulose Nanocrystal), CNT (Carbon Nanotube), SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), FTIR (Fourier Transform Infrared Spectroscopy), NMR (Nuclear Magnetic Resonance), TGA (Thermogravimetric Analysis), DSC (Differential Scanning Calorimetry), DMA (Dynamic Mechanical Analysis), XRD (X-Ray Diffraction), UV (Ultraviolet), H-Bonding (Hydrogen Bonding), MPa (Megapascal), wt.% (Weight Percent), RT (Room Temperature).

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