

## **Nonisocyanate polyurethanes: green solutions**

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At present, many types of polymers of various chemical structures have been developed; on their basis, a huge range of polymeric materials is obtained that meet the needs of various industries. However, among them it is necessary to single out polyurethane, which provides the production of technically important types of polymeric materials. Polyurethane production volumes amounted to 24.7 million tons in 2021. Polyurethanes are high molecular weight compounds with urethane groups  $\text{-NHC(O)O-}$  in the main chain. The macromolecules may also contain ether, ester, urea and other functional groups.

The traditional method for producing polyurethanes is a polyaddition reaction between an aliphatic or aromatic isocyanate containing at least two reactive groups and an oligomeric polyol containing two or more reactive hydrogen atoms. However, the main problem in the production of polyurethanes is the environmental aspect, since polymer precursors - isocyanates, are dangerous for the environment and humans, and their production is based on the use of highly toxic phosgene gas [1-3]. Phosgene, in turn, is produced using toxic gases: chlorine and carbon monoxide. In addition, the released hydrogen chloride requires the use of expensive complex equipment. For this reason, it became necessary to search for alternative environmentally friendly routes for the industrial synthesis of nonisocyanate polyurethanes. The practical application of NIPU based on epoxy-amine compositions and five-membered CCs (1,3,3-dioxolan-2-ones) in coatings, sealants, adhesives, etc. was largely developed back in the USSR by O. Figovsky, V. Stroganov and others in the 1980s-1990s.

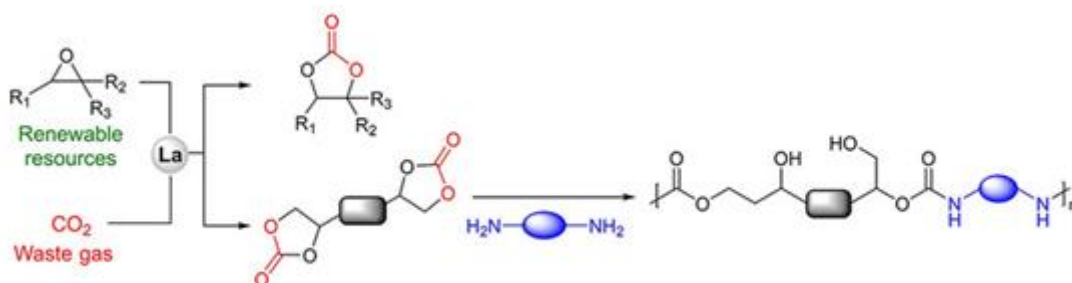
Much of the ongoing research is focused on replacing fossil fuels with renewable alternatives based on plant biomass. In particular, monomers such as carbon dioxide, vegetable oils and carbohydrates, and terpenes have shown excellent performance in the production of various sustainable materials and products. Thus, there is a need to produce high quality polymers from renewable resources while avoiding oil depletion and disposal issues [5-6].

The use of waste greenhouse gases, including carbon dioxide, to produce useful and valuable polymers has long been of interest to researchers, and this chemical process is now on the cusp of commercialization. The process makes it possible to obtain 30–50% of the mass of the polymer from carbon dioxide, and the rest is obtained from oil, which determines economic and environmental benefits [7-8].

Carbon dioxide is common, non-toxic, cheap and versatile. As a greenhouse gas, carbon dioxide contributes to climate change, leading to sea level rise and extreme weather. The concentration of carbon dioxide in the atmosphere due to anthropogenic emissions increases annually by 3.9%. The prospect of using carbon dioxide for polymerization on an industrial scale is obvious: the potential possibility of reducing the amount of carbon dioxide in the atmosphere contributes to the circular economy [9].

The efficiency of the carbon dioxide sequestration process is highly dependent on the catalyst used. In general, homogeneous catalysis provides a much more productive incorporation of carbon dioxide into the polymer chain, resulting in a balanced ratio of epoxide and carbon dioxide and yielding aliphatic polycarbonates. On the contrary, heterogeneous catalysis requires more stringent synthesis conditions and provides a low level of carbon dioxide uptake [9-10]. However, the methods are currently at an early stage of development. The commercialization of the process is associated with the prospects of application. An important advantage of carbon dioxide recycling is the use of existing infrastructure for the petrochemical production of polymers. For example, the polymerization may be carried out using existing reactors and processing and purification methods.

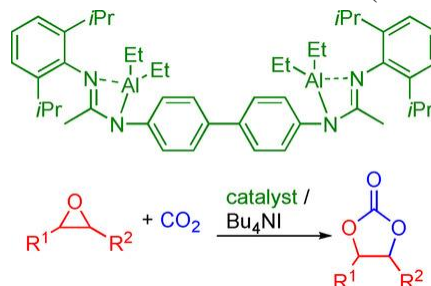
One possible green route for the synthesis of non-isocyanate polyurethanes is the use of functionalized vegetable oil, which has led to a new range of biodegradable, renewable and sustainable sources of NIPU [2]. The synthesis of a wide range of cyclic carbonates from epoxides based on unsaturated acids and CO<sub>2</sub> was efficiently carried out using a lanthanum catalyst. The versatility of this catalyst was confirmed by the synthesis of eleven monosubstituted cyclic carbonates and a bis-cyclic carbonate obtained from epoxidized fatty acid waste products. Then some of the synthesized carbonates were used to obtain polyhydroxy urethanes by reaction with 1,4-diaminobutane (Scheme 1).



Scheme 1. Synthesis of polyhydroxy urethanes

Other researchers have developed a number of inexpensive and stable aluminum amidate complexes as catalysts for the chemical fixation of carbon dioxide into cyclic carbonates. Reactions using terminal epoxides as substrates were

carried out at room temperature and 1 bar carbon dioxide pressure in the presence of tetrabutylammonium iodide as cocatalyst in the absence of solvent. Under these conditions, excellent conversions and selectivity were achieved for a wide range of terminal epoxides. The catalyst has also been used to synthesize disubstituted cyclic carbonates from internal epoxides and carbon dioxide (Scheme 2).



Scheme 2. Synthesis of disubstituted cyclic carbonates from internal epoxides in the presence of aluminum amidate complexes

Aluminum di-metallic complexes (salens) exhibit exceptionally high catalytic activity in the synthesis of cyclic carbonates from terminal epoxides and carbon dioxide at ambient temperature and pressure [12].

Carbonized vegetable oils have been used to produce non-isocyanate polyurethanes: the epoxy group reacts with carbon dioxide to form cyclic carbonates without by-products. The reaction proceeds in the presence of a catalyst, at high pressure and at moderate temperatures. Then carbonized oils interact with polyfunctional amine compounds for the synthesis of polyhydroxy urethanes [12].

Metathesis can be singled out among the possible routes for the functionalization of vegetable oils. Metathesis is the exchange of alkylidene groups between reactants in the presence of ruthenium catalysts. Self-metathesis results in a complex mixture of linear macrocyclic oligomers, cross-linked polymers, and trans/cis isomers that increase the reactivity of the vegetable oil. Cross metathesis with ethylene gives triglycerides with terminal double bonds. The latter route provides advantages: less steric hindrance, no dangling chains (Scheme 3) [13].



Scheme 3. Cross-metathesis of vegetable oil triglycerides

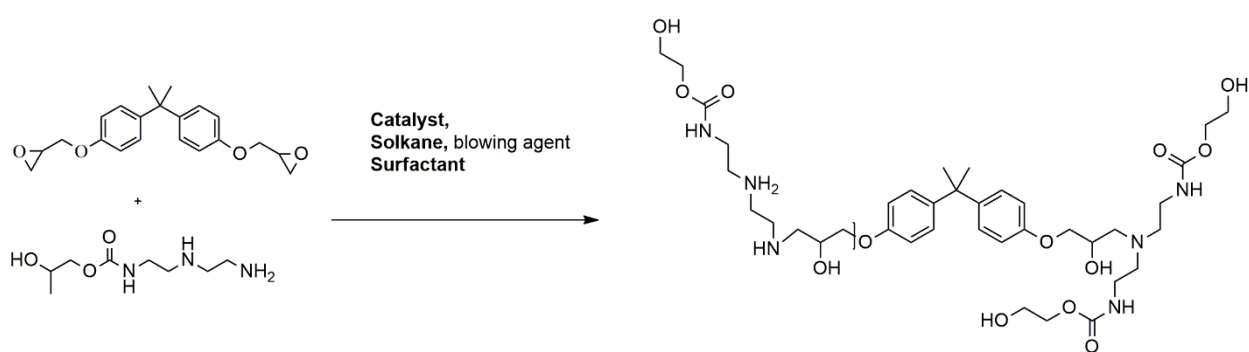
Natural vegetable oils have proven to be effective and show promise as green precursors for NIPU synthesis. Nevertheless, in recent years, in order to expand the initial raw material for the synthesis of NIPU, there are works using other renewable resources, such as terpenes, isosorbide, tannin and lignin derivatives. vanillin and

glycerol. The synthesis of nonisocyanate polyurethanes based on isosorbide monomers with carboxyl functional groups is of considerable interest.

Active research is underway to develop foamed polyurethane foams based on NRPU. However, only isolated solutions are found in the literature. Weak elaboration of the issue is due to the following factors. Firstly, the impossibility of isolating the blowing agent in the reaction of forming NIPU, in contrast to the classical reaction of obtaining polyurethanes, where the release of CO<sub>2</sub>, which forms the foam, occurs directly during the formation of the polymer due to the hydrolysis of the isocyanate group. Secondly, only recently there has been a trend towards state regulation in the field of polyurethanes in order to replace unsafe isocyanates.

The first mention of the possibility of forming foam based on NIPU refers to the US patent 2014/0191156A1. The patent describes the creation of a new cyclic carbonate monomer that can be used as a reactive intermediate for the production of various polymers. The basis for cyclic carbonates in the invention is divinyl arene oxides, which are proposed to be converted into the corresponding carbonates at a temperature of about 100 °C under a CO<sub>2</sub> pressure of about 5 atm, using TBAB as a catalyst. Directly foamed NRPU is proposed to be formed by the reaction of carbonates with the TETA hardener, using cyclohexane as a foaming agent, and surfactant as a foam stabilizer. A method for forming a non-isocyanate composition for spraying, as well as a device for implementing the process and formulations for forming a non-isocyanate foam are presented in US patent 2015/0024138A1.

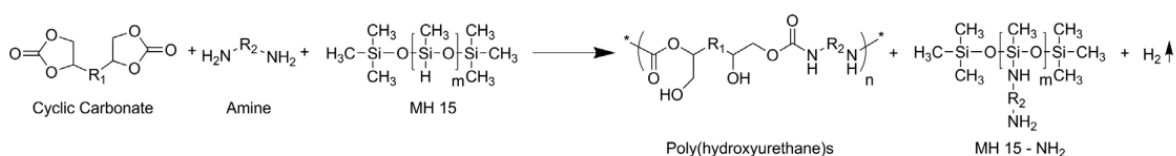
The spray mixture consists of two components fed into a heated mixer. Chemically, this patent is based on the reaction of high epoxy number dianic epoxides and a hydroxyurethane intermediate, according to the scheme 4:



Scheme 4. Obtaining NIPU by the reaction of diene epoxides with hydroxyurethanes

It is essentially a reaction between an epoxy and an amine-type urethane hardener. This, of course, contradicts the general approach to the reaction of cyclocarbonate and amine, but given that epoxides react with amines better than

carbonates, this approach is justified. For the first time in scientific publications, foamed NRPU was obtained from carbonate, i.e. poly(propylene oxide)bis-carbonate and trimethylolpropane tricarbonate and two amines [14]. Equivalent amounts of blowing agent (MH 15) were used for foaming. An outgassing reaction proceeded between the amine groups of the hardener and the SiH groups of MH15 by releasing molecular hydrogen. The synthesized foams are high density elastic foams and their structure and thermal properties depend on the degree of crosslinking provided by the difference in cyclic carbonate functionality and amine structure – see scheme 5..

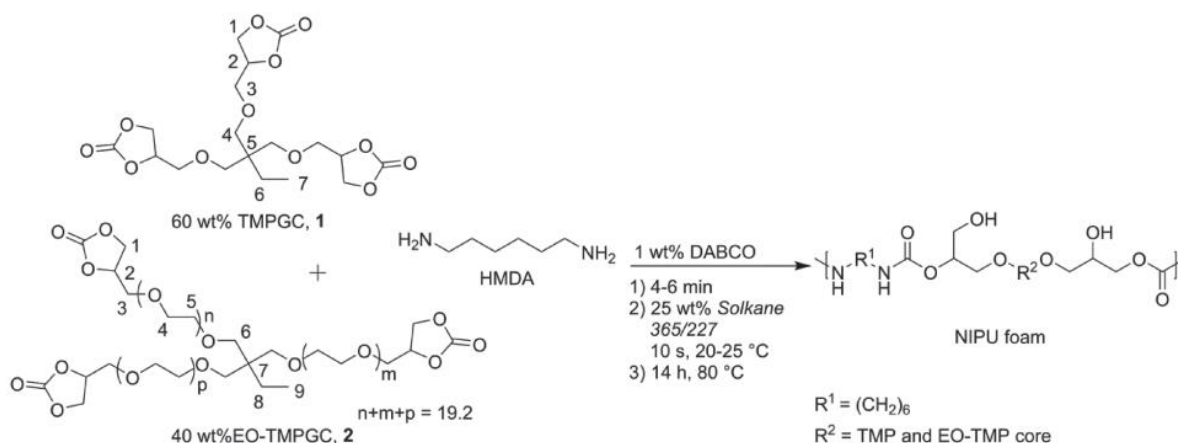


Scheme 5. General scheme for the formation of NIPU foam by the reaction between cyclic carbonate, amine and MH 15

Supercritical CO<sub>2</sub> technology has also been applied to produce foamed NRPU. To this end, cyclocarbonates based on polyethylene glycol diglycidyl ether and epoxidized soybean oil (ESBO) were obtained by CO<sub>2</sub> cycloaddition using a two-component organocatalyst consisting of salt and fluorinated alcohol. NIPU was obtained by stepwise melt polymerization with a biologically derived amine-active oligoamide. Finally, NIPU foams with fine pores (1–20 μm), low density (d ≈ 110 kgm<sup>3</sup>), and rather low thermal conductivity (λ = 50 MW m<sup>-1</sup> K) were obtained by a two-stage periodic foaming method. The method consists of impregnation of NIPU samples with carbon dioxide under supercritical conditions before their expansion at a temperature of 80 °C [15-16].

In the same year, a versatile process was introduced to produce 100% plant-based NIPU flexible foams obtained by curing mixtures of trimethylolpropane-based cyclic carbonates (TMPGC/EO-TMPGC) with HMDA. Freon (Solkan 365/227) was used as an environmentally friendly blowing agent. Blending the flexible EO-TMPGC with the rigid TMPGC significantly improved the handling of the NIPU foam and allowed full control over the properties of the NIPU foam -see the scheme 6. With an increase in the content of EO-TMPGC, the viscosity of the carbonate mixture decreased, which was accompanied by a decrease in the glass transition temperature of NIPU. Thus, it is possible to obtain flexible bio-based NIPU foams for car seats using carbonate mixtures with a composition of 60 wt. % TMPGC and

40 wt. %EO-TMPGC. Presented NIPU flexible foam showed a low density of 83 kg/m<sup>3</sup> [17].



Scheme 6. Preparation of flexible NIPU foams by curing mixtures of TMPGC and ethoxylated TMPGC with HMDA in the presence of fluorocarbon as a physical blowing agent at 80°C for 14 hours.

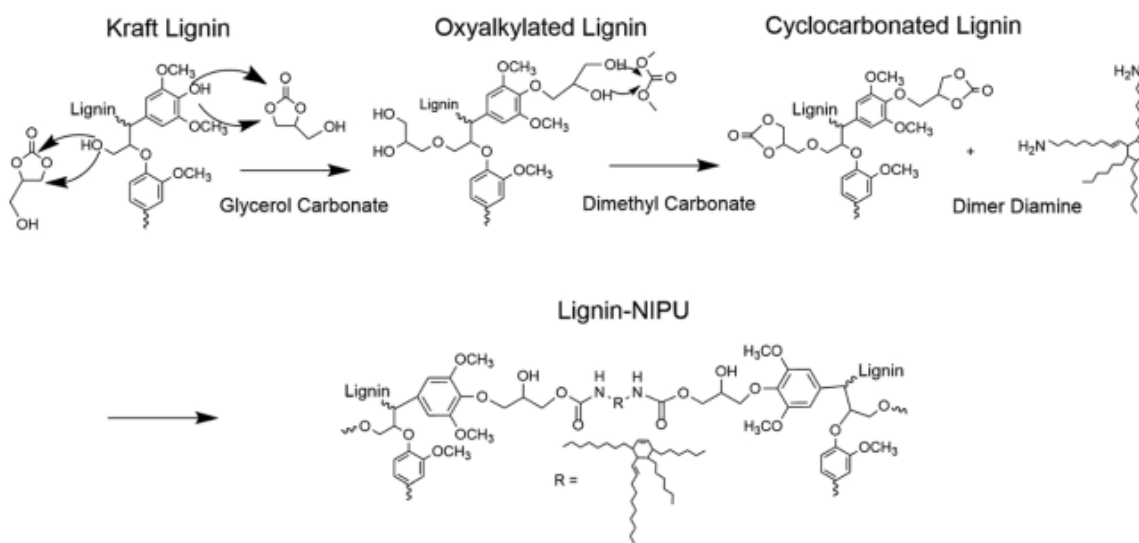
Flexible NIPU foams have a very good hysteresis value of 13.3% combined with a hardness of 3.0 kPa. Unlike modern NIPU blowing agents and silicon-based chemical blowing agents, fluorocarbons are not incorporated into the polymer structure, do not require high pressure, and do not release flammable hydrogen. Since the properties of NIPU are determined solely by the composition of the mixture of carbonates, mixing different carbonates eliminates the need to include less reactive long chain diamines such as Priamine 1047 or Jeffamine, which can cause side reactions due to longer reaction times.

Partially self-inflating and self-curing biobased polyurethane foam from glucose-based non-isocyanate precursors (g-NIPU) was prepared by the reaction of glucose with dimethyl carbonate and hexamethylenediamine [18]. In this work, g-NIPU-based self-inflating foam was prepared at room temperature using maleic acid as an initiator and glutaraldehyde as a cross-linking agent. The resulting self-inflating rigid foams have good resilience, which is directly proportional to the density of the foam. Increasing the amount of glutaraldehyde or decreasing the amount of maleic acid thickens the cell walls and increases the density of the foam.

Another example of an environmentally friendly solution leading to materials entirely from natural raw materials is the production of NIPU from lignin using biomass as a precursor for cyclocarbonates and for hardener. For the first time, a unique non-toxic cyclocarbonation scheme was used. NIPU have been obtained with properties comparable to those of classical cyanate polyurethane. The simplicity and safety of the presented technique open up the possibility of wide application of lignin



chemistry see the scheme 7. The disadvantages of the method include the need to use hydrosilanes for foaming and the overall high density of the resulting foam [16].



Scheme 7. Reaction scheme for functionalization of kraft lignin with cyclic carbonates and curing with diamine based on fatty acids

Despite the published promising results on NIPU foams, the development of exothermic endogenous self-purging approaches that can compete with the versatility and simplicity of isocyanate-based formulations is critical. High temperatures or an external blowing agent are required to stimulate foaming of NRPU foams. The interaction of epoxy oligomers with amines is exothermic. Therefore, with an equimolecular ratio of functional groups, the aminophenol hardener is capable of polymerization "in situ" with the release of volatile products that foam the polymer. The combined use of epoxy oligomers and cyclocarbonates leads to a more uniform distribution of the foamed polymer pores and a decrease in their size. The decrease in the amount of polyalkylaminophenol in relation to the stoichiometric by 30% by weight does not provide foaming of the composition. This is due to the fact that the exothermic effect is not sufficient to release volatile substances. Apparently, the high reaction rate does not allow the formation of uniform pores. It has been established that the use of cyclocarbonates, which have a lower activity in reactions with amines, leads to a decrease in the curing rate. Thus, it is possible to obtain foamed polymers with a more uniform pore distribution.

Polyurethane coatings are widely used in various applications due to their excellent properties, especially hydrolytic stability, high elasticity and good chemical resistance. However, the use of toxic components poses a serious health and environmental hazard in both production and use. In addition to environmental concerns, imperfect coating technology is associated with application and curing

times, as multiple coats are required to meet high performance requirements and achieve the desired final film thickness. In addition, the use of a solvent suggests a long time for complete curing up to 12 hours for. In non-ideal conditions, the curing time is significantly increased to 5-7 days.

Radiation curing technology has been used to rapidly form polymer networks based on NIPU. Recent innovations in UV curing equipment open up the possibility of using such systems on site, which significantly reduces curing time regardless of temperature and humidity. Urethane acrylates provide an exceptional balance of mechanical and chemical properties of coatings and are synthesized by isocyanate-free routes. We are used a composition containing acrylic-based reactive oligomers that was foamed and then polymerized to form a foam with a structure suitable for sealing.

The study [19] describes the synthesis of a series of stable UV-curable non-isocyanate acrylate urethane oligomers (NIPU-AC) with various structures and equivalent acrylate masses, which were used as the main building block of UV-curable coatings for aerospace applications. The results showed that critical performance properties, such as low temperature flexibility and resistance to specific chemicals, were achieved through the selection of appropriate reactive thinners and UV curing conditions.

The development of coatings using water-based polyurethane dispersions that can be cured under ambient conditions has attracted the attention of scientists. The authors have synthesized similar self-oxidizing polyurethane dispersions based on cardanol. Intermediate and final products were studied using FTIR spectroscopy to determine the conformation of the synthesis reaction and their structure. Dried coating films using a suitable desiccant catalyst showed improved mechanical properties and solvent resistance. The corrosion resistance properties of coatings on steel substrates have also shown improved performance for crosslinked films.

A screening study for the production of a rigid polyurethane thermal insulation foam, a protective coating and a casting system based on NIPU showed the suitability of the developed materials for use in space [20]. Synthesis of NIPU was carried out by the reaction of cyclocarbonates with amines without the use of organic solvents and environmentally hazardous foaming agents that deplete the ozone layer (CFC). The best results were obtained with the HNIPU conformal coating and NIPU potting system, which provided performance comparable to reference commercial polyurethanes. The GNIPU foam did not meet the basic technical requirements for use as external thermal insulation for liquid fuel tanks of launchers. However, the quality of the resulting foam allows it to be used on an industrial scale.



In general, the development of coating technologies is driven by the constant need for higher performance to extend service life, reduce maintenance costs, increase efficiency for economic and environmental reasons, health and environmental constraints. One of the most promising areas in this area is smart coatings. To date, they have found application in the automotive industry, construction, consumer electronics, and other areas. Grandview Research estimates that the global market for smart coatings, including self-healing ones, was valued at \$885.5 million in 2015. By 2024, the coatings market will reach approximately \$1 billion.

The first industrial production of NIPU was founded by "Nanotech Industries, Inc." (USA, California). For the development and development of industrial production of non-isocyanate polyurethanes and hybrid materials based on them, the company received the Presidential Green Chemistry Challenge Award in 2015. [22] The award-winning work was carried out under the guidance of the author of the book, at that time director of science and development at Polymate Ltd, Professor Oleg Figovsky. The industrial technology for producing coatings, monolithic floors and foamed polyurethanes that do not contain toxic and carcinogenic isocyanates at all stages of the technological process was also created there for the first time.

In the process of developing "green technology", Polymate Ltd. has developed several cutting-edge technologies protected by more than 10 US, European and Canadian patents. Non-isocyanate polyurethanes are obtained by the reaction of oligomeric cyclocarbonates, including those based on vegetable oils and oligomeric primary amines. Such polyurethanes have high strength, impact and wear resistance, as well as hydrolytic stability. The topic of environmentally friendly industrial nanotechnologies is the main research topic of the Polymate International Nanotechnology Research Center (Israel), which has created more than ten such technologies protected by US patents.

Today, NIPU is being extensively tested and developed in the United States by order of the Department of Defense USA. The objective of this project is to develop and evaluate innovative non-isocyanate polyurethane (NIPU) coating systems for environmentally sustainable rain erosion resistant coatings that meet or exceed the performance requirements specified in SAE AMS-C83231A, as well as some required performance properties in accordance with MIL-PRF-32239. The project will also develop a strategic transition plan for deploying this new technology in the field through joint development with industry partners and end users of US Department of Defense facilities.[21]

A new UV-curable composition is presented by an American developer of industrial coatings, which is the company Hybrid Coating Technologies . It is the first commercial company to produce polyurethane coatings and paint products from

renewable sources under the brand name Green Polyurethane™. Isocyanate-free foam development is still under research, while NIPU-modified hybrid coatings and acrylic polymers are commercially successful.

According to Hybrid Coating Technologies, polyurethane flooring is UV cured in one hour rather than the standard seven days. Thanks to this development, the company's technology was mentioned by the Environmental Protection Agency as an alternative to toxic polyurethanes. The plans of the Agency include in the near future to introduce a ban on the use of isocyanates, which have a negative impact on human health. Despite the similarity of NIPU's chemical structure to conventional polyurethanes, replacing them has proven to be more of a challenge. Despite a huge amount of academic research in this area, the market for alternative NIPUs remains insignificant.

Polyurethanes combine the hardness and rigidity of metals and plastics with the flexibility of rubber. This has made polyurethane the material of choice for many applications from high performance sports cars to household items. Polyurethane also remains a staple in coatings, sealants, adhesives, elastomers, foams, textiles, automotive, the marine industry and even the biomedical industry. The production of a large number of products based on polyurethane with different properties is associated with a wide range of starting components.

Obtaining NIPU by the interaction of amines with cyclic carbonates with the formation of a urethane group remains the preferred method of manufacture. However, advances in the synthesis of cyclic carbonates by chemically incorporating CO<sub>2</sub> into epoxy resins have led to a new round of research in replacing traditional polyurethanes with non-toxic alternatives. Trends in the use of plant precursors for the production of polyurethanes allow the production of "green" products. The development of water-based NIPUs for various applications is also of increasing interest, as the method allows for more environmentally friendly processes and expands the scope of NIPUs. At the same time, the market demand for sustainable plastics production is growing.

The wide distribution of commercial products based on traditional polyurethanes with different properties depending on the composition, as well as 66% of the production of polyurethane in the form of foams, today cannot be replaced by any commercial product based on NIPU. Despite the many benefits of NIPU and extensive academic research, the use of NIPU in industrial applications remains relatively low compared to conventional polyurethanes.

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