

Recent advances in the development of non-isocyanate polyurethanes based on cyclic carbonates

Recent advances in chemistry and technology of non-isocyanate polyurethane (NIPU) materials based on cyclic carbonate oligomers are reviewed in this paper. Reaction of the cyclic carbonate and amino groups results in β -hydroxyurethane fragments with specific properties. Primary attention is given to the hybrid materials that contain epoxy and acrylic compounds, especially materials based on renewable raw materials. Hybrid organic-inorganic composites comprising of silanes are also considered. An overview of the recent publications in this field is provided with a more detailed description of the Polymate Ltd. achievements. The use of NIPU materials as coatings, adhesives, and foams is described.

1. Introduction

Polyurethanes (PU) are among the most used polymers in many modern technologies [1]. However, the use of toxic components, such as isocyanates, in the manufacturing process can render PU production extremely toxic and dangerous [2]. Non-isocyanate sources for PU production have been sought for a long time.

Non-isocyanate polyurethane (NIPU) based on the reaction of polycyclic carbonates and polyamines are known for more than 50 years. Fundamentals for the practical application of NIPU on the basis of five-membered cyclic

carbonates (1,3-dioxolan-2-ones) in coatings, sealants, adhesives, etc. were largely developed by O. Figovsky in the 1970–1980's [3]. Recently, some reviews dedicated to synthesis of cyclic carbonates and NIPU have been presented [4–6]. In these works the advantages of NIPU have been described in detail.

NIPU networks are obtained by the reaction between polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups [4]. This forms a crosslinked polymer with β -hydroxyurethane groups of different structure – polyhydroxyurethane polymer. Since NIPU is obtained without using isocyanates, the process of synthesis is relatively safe for both humans and the environment in comparison to the production of the conventional polyurethanes. The model scheme of the two options β -hydroxyurethane fragments of polymer chains formed in the case of bifunctional starting materials is shown in **figure 1**.

Moreover, NIPU is not sensitive to moisture in the surrounding environment. Hydroxyl groups formed at the β -carbon atom of the urethane moiety also increase adhesion properties. Plurality of intra- and intermolecular hydrogen bonds [7, 8] as well as the absence of unstable biuret and allophanate units [9] seems to be responsible for increased thermal stability and chemical resistance to non-polar solvents.

The mechanism of the reaction of cyclic carbonates with amines, providing non-isocyanate urethanes, was studied by means of quantum chemical calculation in terms of DFT by the PBE/TZ2P method using as examples the reactions of ethylene carbonate and propylene carbonate with methylamine [10, 11]. Structural investigations have revealed four cyclic isomers with intramolecular hydrogen bond and six open conformers. This agrees well with previous results of IR and NMR spectroscopic investigations [4, 7, 8]. The reaction can proceed through the one- or multistage path involving one or two amine molecules. The second amine molecule plays the role of the catalyst of the process, resulting in a substantial decrease in the activation energy of the reaction.

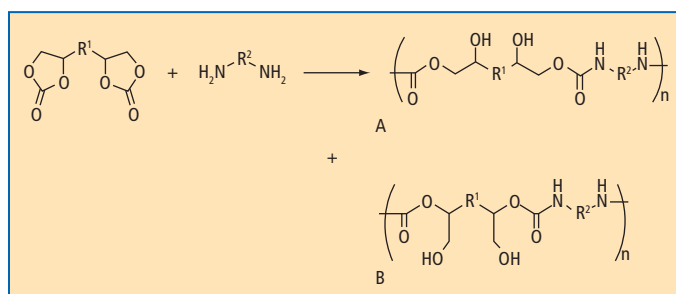
2. Brief description of recent works in the field of NIPU

A significant problem of the NIPU technologies is lack of commercially available multifunctional cyclic carbonates. Recent work in the field of new methods for preparing of cyclic carbonates is dedicated primarily to the development of new catalytic systems and the synthesis of mono-functional compounds [12, 13]. Similar catalyst systems are used also for the copolymerization of epoxides and

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Fig. 1:
 β -hydroxyurethane moieties of non-isocyanate polyurethanes:
A – with secondary hydroxyl groups;
B – with primary hydroxyl groups



CO₂ and ring-opening polymerization of cyclic carbonates [14, 15], and one or the other direction of the reaction depends on the process conditions. For this work the synthesis of mono- and polycyclic carbonates for research purposes were provided by the company Specific Polymers, France [16].

Bernard (Rhodia) proposes a method for preparing polyhydroxyurethanes, which comprises of reacting of at least one compound (1) having a cyclic carbonate functional group and at least one hydroxyl functional group; at least one compound (2) having at least one linear carbonate functional group; at least one compound (3) having at least one primary or secondary amine functional group [17]. The subject of this invention is to position predominantly aqueous formulations on the base of polyfunctionalized polyhydroxyurethane intermediates, as well as creating a method for preparing formulations for use especially in coatings, adhesives, and others. However, the described process is very complicated and time-consuming, requires large amounts of organic solvents, and the formulations for the practical application in most cases require the use of isocyanate-containing components.

Moeller, et al. (Henkel) also describe the bonding agent system that contains a component (A) carrying at least two cyclic carbonate groups and a component (B) carrying at least two amine functional groups to prepare a two-component NIPU adhesive [18]. In this case also component (A) comprises of the reaction product of hydroxyl group-containing cyclic carbonate with an isocyanate group-containing polyurethane pre-polymer. Currently in the coatings industry cyclic carbonate raw materials are often suggested for the use in hybrid epoxy-hydroxyurethane compositions [5]. Use of such systems assumes preliminary production of adducts of the cyclic carbonates and amines. These adducts (also named as amino-urethanes) contain amine, urethane, and hydroxy groups and serve as hardeners for various oligomer compositions. Such compositions, named as Hybrid NIPU (HNIPU), are well-known in the art. Mainly they relate to waterborne epoxy compositions.

Muller-Frischinger (Huntsman Co.) [19] describes a curable composition comprising of: a) mixture of an epoxy resin a cyclic carbonate, and b) as curing agent a hybrid hardener, whereby said hardener is a blend of b1) an aminic compound, and b2) a dicyclopentadiene-phenol based Novolac. Later Muller-Frischinger et al. disclose a curable composition comprising of an epoxy resin and a hybrid hardener; wherein said hybrid hardener is a blend of adduct of amines or amidoamines and monocyclic carbonates (in particular) and a polyphenol Novolac. Such compositions are useful for rapid setting and protective coatings and adhesives in application fields like civil engineering, marine, architectural, and maintenance [20]. Also researches of Huntsman Co. proposed filled compositions on the base of NIPU or HNIPU and nanoclays [21]. In this work cyclic carbonates, synthesized by Polymate Ltd., were used as raw materials.

Klopsch et al. (BASF) disclose the use of new cyclic carbonates with unsaturated bonds as reactive diluents in epoxy resin compositions [22]. It has been found that addition of just small amounts of the new compounds to epoxy resins results in a significant increase in the reactivity of the epoxy resin composition, evident from a lower gel time following addition of a hardener. However, enhancing of other important properties has not been achieved.

Mecfel-Marczewski et al. (Construction Research & Technology GmbH) propose substituted cyclic carbonates – 2-Oxo-1,3-dioxolane-4-carboxylic acid and derivatives thereof. It is assumed that these compounds will be widely used in the oligomer technology [23]. The problem of obtaining NIPU materials based on renewable raw materials is given considerable attention in the research centers of the USA (Wilkes and co-workers, Doll, Erhan, Holser, Javni, Petrović et al.), in Poland (Rokicki and co-workers), and China (Kang, Li et al.) [5].

Recently, a number of European academic centers have begun to actively develop NIPU from the direction of plant-based raw

materials. Thus, researchers at the Institute of Macromolecular Chemistry at the University of Freiburg have investigated soy- and linseed oil-based polyurethanes prepared by curing carbonated soybean (CSBO) and linseed (CLSO) oils with different diamines [24]. Later they have reported on a very versatile new route to linear as well as crosslinked terpene-based non-isocyanate poly(hydroxyurethanes) (NIPU) and pre-polymers derived from the novel cyclic limonene dicarbonate (CL) [25]. The catalytic carbonation of epoxidized limonene with CO₂ was monitored in the presence of both homogeneous tetrabutylammonium bromide (TBAB) and heterogeneous silica supported 4-pyrrolidinopyridinium iodide (SiO₂(I)) catalysts. The systematic variation of catalyst type, CO₂ pressure and temperature enabled quantitative carbonation in bulk and incorporation of 34.4 wt% CO₂ into CL. In contrast to conventional plant oil-based cyclic carbonates, such terpene-based cyclic carbonates afford much higher CO₂ fixation and do not contain ester groups. The absence of ester groups is essential to prevent side reaction with amines: ester groups react with the amine curing agent to afford amides and low molecular weight polyol by-products which can cause undesirable emissions and plastification of NIPU. Novel linear NIPU and prepolymers were obtained by means of CL advancement with diamines such as 1,4-butane diamine (BDA), 1,6-hexamethylene diamine (HMDA), 1,12-dodecane diamine (DADO), and isophorone diamine (IPDA).

Cramail et al. (University of Bordeaux) reported polyaddition of diamines with vegetable-based biscarbonates to prepare new polyurethanes. The intermediate material (epoxidized compounds) were obtained in two steps by a transesterification starting from monoalkyl esters of unsaturated acids and diols, and subsequent epoxidation. Then the biscarbonates were prepared from difunctional epoxides and supercritical CO₂ in the presence of ionic liquids and tetrabutylammonium bromide (TBABr) as the catalyst. Received cyclic carbonates were considered as polyhydroxyurethane precursors and further self-polycondensed with ethylene

diamine and isophorone diamine to form polyurethanes [26]. For preparation of bis-carbonates with terminal cyclic carbonate groups were used in a metathesis reaction with Hoveyda's catalyst.

Researchers from Reutlingen University and the University of Natural Resources and Life Sciences of Vienna obtained a new bio-based non-isocyanate urethane by the reaction of a cyclic carbonate synthesized from a modified linseed oil and an alkylated phenolic polyamine (phenalkamine) from cashew nut shell liquid. The incorporation of functional cyclic carbonate groups to the triglyceride units of the oil was done by reacting epoxidized linseed oil with CO₂ in the presence of a catalyst. Structural changes and changes in molar mass during the carbonation reaction were characterized. Also the aminolysis reaction of the cyclic carbonate with phenalkamine was monitored, as well as the viscoelastic properties of the system and the time of gelation [27].

A novel bio-based, isocyanate-free poly-(amide urethane) derived from soy dimer acids is described. Three steps are involved in this one-pot synthesis: first, dimer fatty acids are condensed with ethylene diamine to produce amine-terminated oligomers intermediates. These intermediates are then reacted in a second step with ethylene carbonate to yield hydroxyl-terminated di-urethanes, which then undergo a transurethane polycondensation at 150 °C for 9 h under vacuum to produce high molecular weight polymers [28]. Although the polymers are produced at a high temperature, above properties still do not allow them to find a practical application.

There is continuous development being made in the direction of silicon-contained

and nano-structured hydroxyurethane compounds. Turkish researchers synthesized a novel carbonate-modified bis(4-glycidyloxy phenyl) phenyl phosphine oxide (CBGPPO) for preparing non-isocyanate polyurethane/silica nanocomposites. Spherical silica particles were prepared and modified with cyclic carbonate functional silane coupling agent to improve the compatibility of silica particles and organic phase. The phosphine oxide-based and cyclic carbonate-modified epoxy resins and silica particles were used to prepare hybrid coatings using diamine as a curing agent. No damage was observed in the impact strength of the coatings. Incorporation of silica and CBGPPO into formulations increased modulus and hardness of the coating making the material more brittle. It was also observed, that the thermal stability of hybrid coatings enhanced with the addition of silica and CBGPPO [29].

A novel bis-urethane organosilane precursor has been developed via NIPU route in sol-gel processing conditions and employed as an organic precursor of organic-inorganic hybrid (OIH) coating systems. Coating formulations with variable proportions of this organic component were prepared and applied on aluminum substrate. These coatings were evaluated for mechanical, chemical properties and corrosion resistance and showed some improvements [30].

Hanada et al. disclose a polysiloxane-modified polyhydroxy polyurethane resin being derived from a reaction between a five-membered cyclic carbonate polysiloxane compound (**fig. 2**) and an amine compound, its production process and a resin composition. New materials can be used for thermal recording medium, imitation leather, thermoplastic polyolefin resin skin material, weather strip material, and weather strip [31].

3. Recent achievements of Polymate Ltd.

3.1 Polyhydroxyurethanes

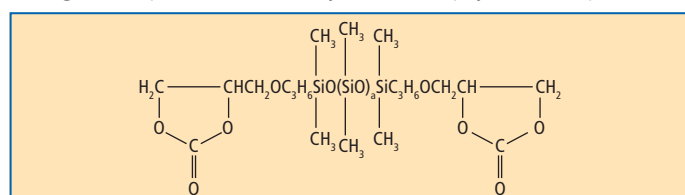
Usually polyhydroxyurethane polymers have poor water resistance due to the plurality of hydroxyl groups. It is however possible to prepare water-resistant materials in some formulations. For example, on the base of acrylic epoxy oligomers, cyclocarbonate acrylic polymers with high water and weather stabilities were prepared. A paint was developed with curing temperature 110 °C, in 2–3 hours. Unfortunately we need to use solvents for this composition [4].

Polymate Ltd. recently started works on the synthesis of aliphatic multifunctional cyclic carbonates from corresponding epoxies and carbon dioxide and NIPU based on them. The authors tested some compositions of polyfunctional carbonates synthesized in the laboratory, namely trimethylol propanetri-cyclocarbonate (TMPTCC) and chlorine containing aliphatic tricyclocarbonates (on the base of chlorine containing aliphatic epoxy resins Oxilin) and various diamines: 2-methylpentamethylene diamine (MPMD) – Dytek A, Invista Co.; meta-xylenediamine (MXDA) – Mitsubishi Gas Chem. Co.; polyetheramine Jeffamine EDR-148 – Huntsman Co.; diethylenetriamine (DETA) – D.E.H. 20, Dow Chemical Co. Properties of these materials are shown in **table 1**. Some of the results are significantly higher than previously achieved levels and offer good prospects for their practical use. Further elaboration will be undertaken.

3.2 Hybrid non-isocyanate polyurethanes

Recently the authors proposed compositions based on oligomer systems which contain

▼ **Fig. 2:** Example of five-membered cyclic carbonate polysiloxane compound



▼ **Tab. 1:** Properties of polyhydroxy urethanes

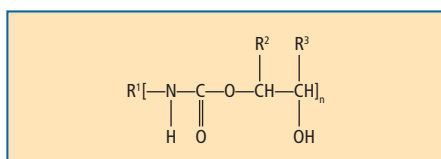
CC	Amine	Tensile strength / MPa	Elongation / %	Water absorption / %
TCCTMP	MPMD	33–47	3.3–3.8	n/a
CC Oxilin 5	MXDA	18	4	n/a
CC Oxilin 6B	EDR-148	0.8	10	4.0
CC Oxilin 6	DETA	1.6	16	n/a

hydroxy-amine adducts on the base of aliphatic mono- and polycyclic carbonates (Cycloate A) as hardeners [32]. This composition was used for 100 % solid flooring coating with high abrasion resistance and mechanical properties. Thus, Polymate has developed practically used formulations on the basis of HNIPU, using the two formulations F1 and F2 shown in **table 2**.

3.3 Hydroxyurethane modifiers (HUM)

A separate area of the use of NIPU technology is in the preparation of pure hydroxyalkyl urethane compounds. All known polymer compositions with hydroxyalkyl urethane monomers require specific chemical reactions (such as transesterification, transamination, or self-crosslinking). These reactions are

Fig. 3: Basic formula of hydroxyalkyl-urethane modifier (HUM)



carried out at elevated temperatures, in the presence of organic solvents, and/or in water-dispersion media, sometimes in the presence of catalysts [5]. The authors recently proposed a novel concept of generating new multifunctional modifiers. The HUM, which possesses a wide range of hydrogen bonds, is embedded in an epoxy polymer network without a direct chemical interaction.

Our patent application [33] discloses a novel "cold" cure epoxy-amine composition modified with a hydroxyalkyl urethane (HUM), which is obtained as a result of a reaction between a primary amine (C1) and a monocyclocarbonate (C2), wherein modifier (C) is represented by the formula in **figure 3**, wherein R1 is a residue of the primary amine, R2 and R3 are the same or different and are selected from the group consisting of H, alkyl, hydroxyalkyl, and n satisfies the following condition: $n \geq 2$. Diluents, pigments, and additives can be used. The new modifier primarily affects a significant acceleration of the curing process as well as an increase in abrasion resistance. Doping with the HUM imparts to the cured composition superior coating performance

characteristics (pot life/drying, strength-stress properties, bonding to a variety of substrates, appearance in a well-balanced state). Since the structure of the polymer network is not broken, other characteristics, such as weathering and chemical resistance, do not worsen. The dependences of curing characteristic and abrasion resistance from content of HUM-01 are shown in **figure 4** [34]. The following sections provide examples of successful applications of HUM into other oligomeric systems.

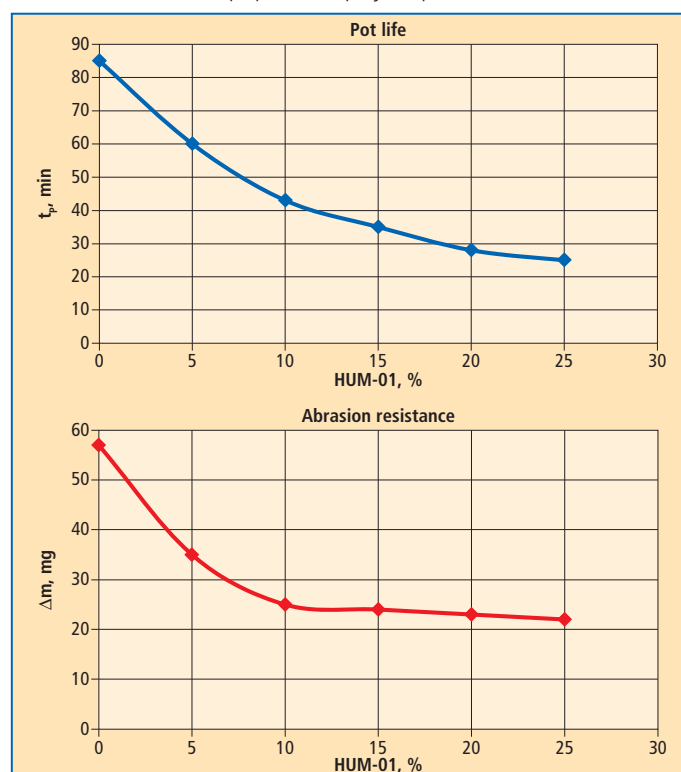
3.4 Hydroxyurethane compounds from renewable plant-based raw materials

Recently authors proposed a new method of producing a hybrid polyhydroxyurethane network comprising of [35]: (a) reacting epoxidized unsaturated fatty acid triglycerides with carbon dioxide in the presence of a catalyst to obtain carbonated-epoxidized unsaturated fatty acid triglycerides, wherein conversion of oxirane groups to 2-oxo-1,3-dioxolane groups (cyclic carbonate groups) for said carbonated-epoxidized unsaturated fatty acid triglycerides ranges from 35 % to 85 % (see **figure 5**);

Tab. 2: Composition and properties of flooring compounds

Composition	Parts by weight	
	F1	F2
Hydroxyl-amine adduct "1" (on the base of Cycloate A)	50.0	–
Hydroxyl-amine adduct "2" (on the base of Cycloate A)	–	50.0
Epoxy resin D.E.R. 324 of Dow Chemical	45.0	40.0
Polycyclic carbonate Cycloate A	5.0	–
Reactive acrylic oligomers (mixture) of Sartomer	–	10
Titanium dioxide	5.0	5.0
Carbon black	–	0.1
BYK-A530 (surface active additive of Byk Co.)	2.0	–
BYK-320 (surface active additive of Byk Co.)	–	1.5
Properties	Values	
Mixed viscosity, 25 °C, mPa·s	1,450	970
Pot life, 25 °C, min	30–60	30–60
Tack free, 25 °C, h	4	6
After seven days room temperature, substrate – concrete		
60° film gloss	100–105	115–120
Hardness / Shore D	70–80	70–80
Tensile strength / MPa	50–60	60–70
Elongation at break / %	5–7	3–4
Taber abrasion, 1,000 cycles/1,000 g, CS-17 wheel / mg	27	29
Impact resistance / N.m, ≥	20	20

Fig. 4: Influence of modifier HUM-01 (trimethyl-hexamethylene-diamine + propylene carbonate) on the properties of epoxy composition based on D.E.R. 331



(b) mixing and reacting the carbonated-epoxidized unsaturated fatty acid triglycerides with a compound having an amine functionality comprising at least one primary amine group realized at stoichiometric or within nearly balanced stoichiometry; (c) mixing and reacting the product of (b) with a compound having amine functionality comprising at least two primary amine groups realized at excess of an amine-functional compound; (d) mixing the product of (c) with a compound having amino-reactive groups and selected from the group comprising: (1) a compound having epoxy functionality, and (2) a mixture of the compound having epoxy functionality with carbonated-epoxidized unsaturated fatty acid triglycerides, a ratio of the sum of amino-reactive groups to the sum of amine groups being stoichiometric or within nearly balanced stoichiometry; and (e) curing the resulting composition at ambient temperature. The proposed method can significantly reduce time of synthesis and improve quality of the final products.

3.5 Silane-containing and nano-structured hydroxyurethane compounds

The concept of generating silica from alkoxysilanes by the sol-gel method within a macromolecular organic phase (in situ) is widely known in the art. The organic and inorganic components of these materials are present as co-continuous phases of a few nanometers in lateral dimensions. Earlier authors have studied new types of NIPUs based on cyclic carbonate-epoxy resin systems and aminoalkoxysilanes [36]. The proposed dendro-aminosilane hardeners give the possibility for the introduction of siloxane fragments into the aromatic structure of BPA epoxy-amine and cyclocarbonate network polymers which improves the service properties of the network polymer. Additional hydrolysis of organosilane oligomers creates a secondary nano-structured network polymer.

Known in the art as hybrid organic-inorganic compositions include mixtures of epoxy resins, amine hardeners, functional silanes, and/or polysiloxanes and cure in the presence of water in an amount sufficient to bring about substantial hydrolytic polycondensation of the silane [5].

A novel nano-structured hybrid polymer composition was synthesized on the base of epoxy-functional components, cyclic carbonate components, amine-functional components, and acrylate (methacrylate) functional components, wherein at least one epoxy, amine, or acrylate (methacrylate) component contains alkoxysilane units [37]. The composition is highly curable at low temperatures (approximately 10–30 °C) with generating nanostructure (fig. 5) under the influence of the forming of active, specific hydroxyl

groups by reaction of cyclic carbonates with amine functionalities. These hydroxyurethane functionalities activate by hydrolytic polycondensation of alkoxysilanes by means of atmospheric moisture, thus producing an organic-inorganic nanostructure without a special procedure of water embedding or addition of nanofillers. The cured composition (fig. 6) has excellent strength-stress properties, adhesion to a variety of substrates, appearance, and resistance to weathering, abrasion, and solvents.

Fig. 5: Obtaining carbonated epoxidized unsaturated fatty acid triglycerides

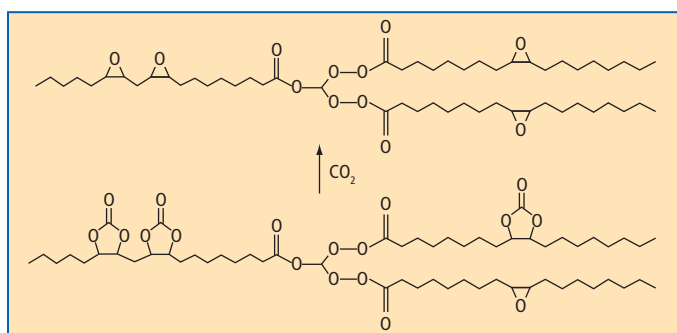
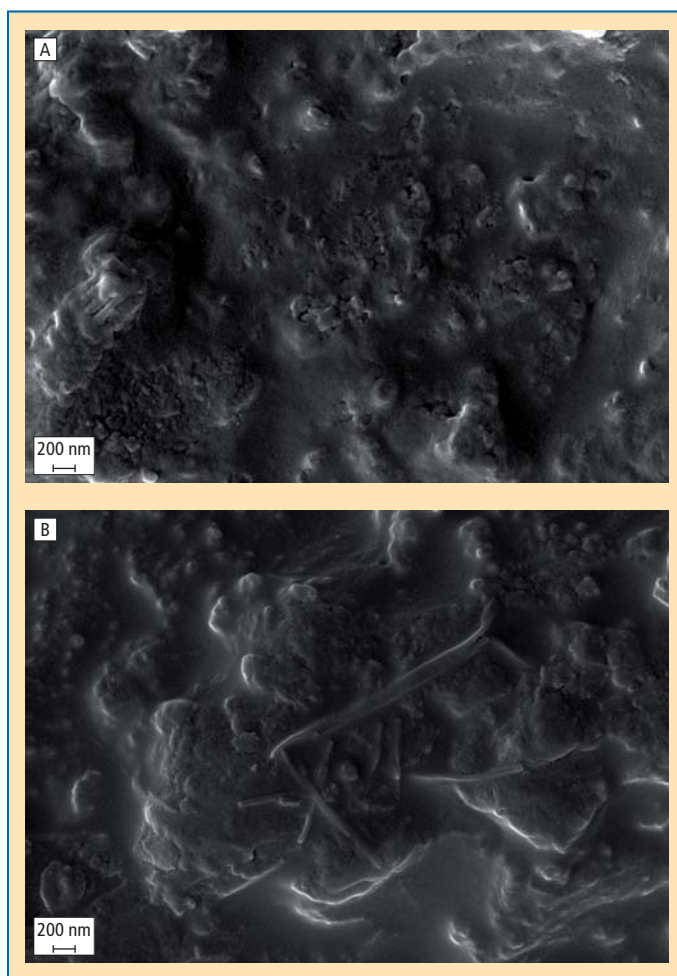


Fig. 6: Images of the fractured surfaces of the cured compositions at 20,000x magnification (Auriga Cross-Beam): A – neat epoxy-amine composition; B – epoxy-silane-amine composition



3.6 Sprayable foam

The vast majority of methods for the application of sprayable polymer foams onto various substrates use air or airless spraying equipment. The main advantage of these methods is the rapid formation of a polymer structure to obtain a non-flowing foam on vertical surfaces. However, non-isocyanate resin foams require some other approach since they exhibit longer durations of gelation and solidification, which can lead to flow on vertical surfaces and a collapse of the foam.

Recently, Olang (Owens Corning) disclosed hybrid spray foams that use a urethane reactant, a crosslinker, and an (optional) epoxy and/or acrylic resin, along with a blowing agent and rheology modifier to produce a quick-setting foam that remains in place until the foam forms and cures [38]. In some other formulations the author used the NIPU

adducts of cyclic carbonates and di- or polyamines, received from Polymate. Unfortunately, the use of rheology modifiers in practice increases the viscosity of the compositions and imparts to them a thixotropic property, which significantly limits the use of this method for spray foams.

Earlier, we described some non-isocyanate compositions related to hybrid systems on the basis of epoxy, hydroxyurethane, acrylic, cyclic carbonate, and amine raw materials in different combinations. Patent [39] discloses foamable, photopolymerizable liquid acrylic-based compositions for sealing applications, which include products of reaction of non-isocyanate urethane diols with methacrylic or acrylic anhydride. Patent [40] describes hybrid non-isocyanate foams and coatings on the basis of epoxies, acrylic epoxies, acrylic cyclocarbonates, acrylic hydroxyurethane oligomers, and bifunctional amines. However, all these compositions are used

“in-place” (in situ) and are unsuitable for spray applications.

Finally, Polymate has developed a basic formulation and technique for mixing and foaming insulating spray foam and a procedure for obtaining conventional foams has been updated in respect to HNIPU application [41]. Technical specifications of this newly developed composition correspond to the mean values of a similar urethane-based thermal insulation. The ultimate strength of the new material is about 1.5 times higher than that of the polyurethane foam, and the heat-insulating properties are at the same level as in polyurethane foam with open cell structures. The possibility of application by spraying was tested on pilot equipment.

Recently the composition of the foam was studied with regards to the use of renewable raw materials, including new HUM. As a result, hard and elastic foams were obtained with properties not inferior to polyurethane foams. The foams were produced in the laboratory only but offered reasonable properties (tab. 3). Research and development of new foams is expedient and can be continued.

3.7 UV curable HNIPU floorings and coatings

The photochemistry involved in UV curable materials is very complicated and usually is tailored to the specific process with its method of application, UV source, pigments, and desired properties of the cured material. UV curable concrete floor coatings offer a durable, high-performance and eco-friendly opportunity for UNIPU chemistry. These thin-film coating systems cure instantly, thereby minimizing the downtime of any facility. Other benefits include excellent chemical resistance, easy cleanability, little odour, and the ability to coat in cold conditions.

The surface preparation and application of UV coatings is similar to that of traditional concrete floor coatings. UV coating systems include both clear and pigmented systems. The clear system consists of a primer and a topcoat, which is available in different finishes ranging from high gloss to matte. The

▼ Tab. 3: Rigid HNIPU foam

Properties	Standard	Rigid foam insulation
Viscosity (Brookfield RVDV II, Spindle 29, 20 rpm) at 25 °C, cP Base "A" Base "B" "A" + "B" (3–5 s after mixing)	ASTM D2393	2,800–3,200 3,600–4,100 ≤ 3.700
Pot life at 25 °C (77 °F) / s		8 – 10
VOC	ASTM D2369	Compliant
Gel time / s Touch dry / s Curing for transportation / min		2–4 30–40 15–20
Appearance of rigid foam		White
Compressive properties of rigid cellular plastics, 24 h / MPa	ASTM D 1621	0.2–0.4
Apparent density of rigid cellular plastics / kg/m ³	ASTM D2794	30–40
Thermal transmission properties by means of the heat flow meter apparatus, h·ft ² °F /Btu.in	C 518	4.5–5.0

▼ Tab. 4: Properties of HNIPU UV-cured flooring compared to conventional UV-cured flooring

Properties	Standard	Conventional UV-cured flooring	HNIPU UV-cured flooring
Adhesion	ASTM D 3359-07, B	3B	5B
Pencil hardness	ASTM D 3363-05	3H	4H
Solvent resistance	ASTM D5402-06	200+	200+
Gloss	ASTM D 523	84	90
Abrasion resistance, CS-17, 1,000 g, 1,000 cycles, mg	ASTM D1044	150–200	100
Thickness applied / mm		0.065–0.1	0.3–0.8
Primer		Required	Not required for properly prepared substrates
Number of layers		2+	1

topcoat finish can be further enhanced by broadcasting additives for decorative or performance purposes.

Single-coat systems are also available. The thin film thickness can range between 0.3 mm and 0.8 mm. Unlike conventional UV curable coatings, formulations developed by Polymate Ltd. contain up to 60 % of vegetable oil derivatives, such as modified soybean oil. This creates a composition with higher elasticity while maintaining the basic strength characteristics. The use of these compounds improves the adhesion of the cured composition to concrete, allowing reduction in the number of coating layers to two, and for special coatings even to a single layer. The uniqueness of this compound is the possibility to apply one layer up to 0.8 mm thickness, at the rate of polymerization which allows the use of standard curing technology and standard equipment. The introduction of the new hydroxyurethane modifier (HUM) based on vegetable raw materials and adducts obtained on its basis allow improving hardness and wear resistance, while maintaining the other properties of the system (tab. 4).

The uniqueness of the developed formulation and the possibility of coating concrete sometimes without a primer, with a layer thickness of 0.3–0.8 mm allows the covering of even open areas. Application is done by spraying, eliminating the negative effects of sunlight during the coating process and uses sunlight during the curing process, which reduces the total polymerization time even more.

4. Conclusions

Many well-known companies and research centres around the world are developing new methods for the synthesis of cyclic carbonates and compositions thereof. A leading position in the development of non-isocyanate materials is being held by the research center Polymate Ltd. The authors believe that further developments in the field of polyhydroxyurethanes, that offer the most promising directions for future research include:

- Creation of production of polyfunctional cyclocarbonates, development of optimal technology and equipment: carbonized vegetable oils and terpenes; carbonized aliphatic compounds, including chlorinated ones; and carbonized polyfunctional silicones.
- Development of waterborne HNIPU formulations.
- Development of NIPU formulations for sealants and adhesives.
- Development of production of amines modified with hydroxyurethane groups.
- Elaboration of non-amine RT curing agents for oligomer compositions.
- Development of self-extinguishing compositions of HNIPU.
- Development of silicone-based HNIPU.
- Development of NIPU and HNIPU-based foams.
- Development of formulations for UV-cured compositions.

5. References

[1] Thomson T. Polyurethanes as specialty chemicals: principles and applications. CRC Press, 2005. 190 p.

[2] Meier-Westhues U. Polyurethanes: coatings, adhesives and sealants. Vincentz Network GmbH & Co KG, Hanover, 2007, 344 p.

[3] Figovsky O. et al. Soviet Union patents: SU529197, 1976; SU563396, 1977; SU628125, 1978; SU630275, 1978; SU659588, 1979; SU671318, 1984; SU707258, 1984; SU903340, 1982; SU908769, 1982; SU1126569, 1984; SU1754747, 1992; SU1754748, 1992.

[4] Figovsky O., Shapovalov L. Cyclocarbonate Based Polymers Including Non-Isocyanate Polyurethane Adhesives and Coatings. Encyclopedia of Surface and Colloid Science, ed. P. Somasundaran, V. 3, 1633–1653. NY, Taylor & Francis, 2006.

[5] Leykin A., Beilin D., Birukova O., Figovsky O., Shapovalov L. Non-isocyanate polyurethanes based on cyclic carbonate: chemistry and application (review), Scientific Israel – Technological Advantages 2009, 11 (3–4), 160–190.

[6] Guan J., Song Y., Lin Y., Yin X., Zuo M., Zhao Y., Tao X., Zheng Q. “Progress in Study of Non-isocyanate Polyurethane”, Ind. Eng. Chem. Res. 2011, 50, 6517–6527.

[7] Rappoport L. Ya., Petrov G. N., Trostyanskaya I. I., Gavrilova O. P. Polyurethane elastomers obtained without the use of diisocyanates. Inter. Polymer Sci. Technol., 1981, 8 (5), T/68-T/70.

[8] Yagund E. M., Maklakov L. I., Stroganov V. F., Savchenko V. N. Studies of hydrogen bonds in model urethane compounds obtained by the “cyclocarbonate – amine” reaction. J. Appl. Spectroscopy, 1987, 45 (1), 737–741.

[9] Tomita H., Sanda F., Endo T. Structural Analysis of Polyhydroxyurethane Obtained by Polyaddition of Bifunctional Five-Membered Cyclic Carbonate and Diamine Based on the Model Reaction. J. Polymer Sci. A, 2001, 39, 851–859.

[10] Zabalov M. V., Tiger R. P., Berlin A. A. Reaction of cyclocarbonates with amines as an alternative route to polyurethanes: A quantum-chemical study of reaction mechanism. Doklady Chemistry, 2011, 441 (2), 355–360.

[11] Zabalov M. V., Tiger R. P., Berlin A. A. Mechanism of urethane formation from cyclocarbonates and amines: a quantum chemical study. Russian Chemical Bulletin, 2012, 61 (3), 518–527.

[12] North M., Pasquale R., Young C. Synthesis of cyclic carbonates from epoxides and CO₂. Green Chem., 2010, 12, 9, 1514–1539.

[13] Pescarmona P. P., Taherimehr M. Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO₂. Catal. Sci. Technol., 2012, 2 (11), 2169–2187.

[14] Kember M. R., Buchard A., Williams C. K. Catalysts for CO₂/epoxide copolymerization. Chem. Commun., 2011, 47, 1, 141–163.

[15] Guillaume S. M., Carpentier J.-F. Recent advances in metallo/organocatalyzed immortal ring-opening polymerization of cyclic carbonates. Catal. Sci. Technol., 2012, 2, 898–906.

- [16] <http://www.specificpolymers.fr/medias/downloads/nipur.pdf>
- [17] Bernard J.-M. Method for preparing polyhydroxy-urethanes. US Patent 8,017,719, 2011; US Patent Application 2011/0288230, 2011.
- [18] Moeller T., Kinzelmann H.-G. Two-component bonding agent. US Patent 8,118,968, 2012.
- [19] Muller-Frischinger I. Coating system. US Patent 8,003,737, 2011.
- [20] Muller-Frischinger I., Gianini M., Volle J. Coating system. US Patent 8,263,687, 2012.
- [21] Diakoumakos C. D., Kotzev D. L. Nanocomposites based on polyurethane or polyurethane-epoxy hybrid resins prepared avoiding isocyanates. US Patent 8,143,346, 2012; Diakoumakos C. D., Kotzev D. L. Non-Isocyanate-Based Polyurethane and Hybrid Polyurethane-Epoxy Nanocomposite Polymer Compositions. US Patent Application 2012/0149842, 2012.
- [22] Klopsch R., Lanver A., Kaffee A., Ebel K., Yu M. Use of cyclic carbonates in epoxy resin compositions. US Patent Application 20110306702, 2011.
- [23] Mecfel-Marczewski J., Walther B., Mezger J., Kierat R., Staudhamer R. 2-Oxo-1,3-dioxolane-4-carboxylic acid and derivatives thereof, their preparation and use. US Patent Application 20110313177, 2011.
- [24] Bähr M., Mülhaupt R. Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion. *Green Chem.*, 2012, 14 (2), 483–489.
- [25] Bähr M., Bitto A., Mülhaupt R. Cyclic limonene dicarbonate as new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes. *Green Chem.*, 2012, 14 (5), 1447–1454.
- [26] Cramail H., Boyer A., Cloutet E., Gadenne B., Alfos C. Bicarbonate precursors, method for preparing same and uses thereof. US Patent Application 2012/0259087, 2012; Foltran S., Maisonneuve L., Cloutet E., Gadenne B., Alfos C., Tassaing T., Cramail H. Solubility in CO₂ and swelling studies by in situ IR spectroscopy of vegetable-based epoxidized oils as polyurethane precursors. *Polym. Chem.*, 2012, 3 (2), 525–532.
- [27] Mahendran A. R., Aust N., Wuzella G., Müller U., Kandelbauer A. Bio-based non-isocyanate urethane derived from plant oil. *J. Polymers and the Environment*, 2012, 20 (4), 926–931.
- [28] Hablot E., Graiver D., Narayan R. Efficient synthesis of bio-based poly(amide urethane)s via non-isocyanate route. *PU Magazine International*, 2012, 9 (4), 255–257.
- [29] Hoşgör Z., Kayaman-Apohan N., Karataş S., Menciloçlu Y., Güngör A. Preparation and characterization of phosphine oxide based polyurethane/silica nanocomposite via non-isocyanate route. *Prog. Org. Coat.*, 2010, V. 69, No. 4, 366–375.
- [30] Kathalewar M., Sabnis A. Novel Bis-Urethane Bis-silane Precursor Prepared via Non-Isocyanate Route for Hybrid Sol-Gel Coatings. *Int. J. Sci. Eng. Res.*, 2012, 3 (8), 1–4.
- [31] Hanada K., Kimura K., Takahashi K., Kawakami O., Uruno M. Five-membered cyclic carbonate polysiloxane compound. Polysiloxane-modified polyhydroxy polyurethane resin. US Patent Applications: 20120231184, 20120232289, and 20120237701, 2012.
- [32] Birukov O., Beilin D., Figovsky O., Leykin A., Shapovalov L. Liquid oligomer composition containing hydroxy-amine adducts and method of manufacturing thereof. US Patent Application 2010/0144966, 2010.
- [33] Birukov O., Figovsky O., Leykin A., Shapovalov L. Epoxy-amine composition modified with hydroxyalkyl urethane. US Patent 7989553 B2, 2011.
- [34] Figovsky O., Birukov O., Shapovalov L., Leykin A. Hydroxyurethane modifier as effective additive for epoxy matrix. *Scientific Israel – Technological Advances* 2011, 13 (4), 122–128.
- [35] Birukov O., Figovsky O., Leykin A., Potashnikov R., Shapovalov L. Method of producing hybrid polyhydroxyurethane network on a base of carbonated-epoxidized unsaturated fatty acid triglycerides. US Patent Application 20120208967, 2012.
- [36] Figovsky O., Shapovalov L., Buslov F. Ultraviolet and thermostable non-isocyanate poly-urethane coatings. *Surface Coatings International Part B: Coatings Transactions*, 2005, 88 (B1), 67–71.
- [37] Birukov O., Beilin D., Figovsky O., Leykin A., Shapovalov L. Nanostuctured hybrid oligomer composition. US Patent 7,820,779 B2, 2010.
- [38] Olang F. N. Hybrid polyurethane spray foams made with urethane prepolymer and rheology modifiers. US Patent Application 2012/0183694, 2012.
- [39] Figovsky O., Shapovalov L., Potashnikov R., Tzaid Yu., Bordado J., Letnik D., De Schijuer A. Foamable photopolymerized composition. US Patent 6,960,619 B2, 2005.
- [40] Figovsky O., Shapovalov L. Preparation of oligomeric cyclocarbonates and their use in non-isocyanate or hybrid non-isocyanate polyurethanes. US Patent 7,232,877 B2, 2007.
- [41] Figovsky O., Potashnikov R., Leykin A., Shapovalov L., Sivokon S. Method for forming a sprayable non-isocyanate foam composition. US Application No.: 13/770,319; filed: 19 February 2013.