

# Progress in elaboration of nonisocyanate polyurethanes based on cyclic carbonates

O. Figovsky, L. Shapovalov, A. Leykin, O. Birukova, R. Potashnikova

Polymate Ltd. – International Nanotechnology Research Center, Migdal HaEmek, Israel

Аннотация: В статье дается обзор производства и применения неизоцианатных полиуретанов на основе циклических карбонатных олигомеров. Неизоцианатные полиуретановые (NIPU) сети получают путем реакции между полициклическими карбонатными олигомерами и алифатическими или циклоалифатическими полиаминами с первичными аминогруппами. Это формирует сшитый полимер с β-гидроксиуретановыми группами различного строения - полигидроксиуретановый полимер. Он рассматривается как надлежащий неизоцианатный полиуретановый и гибридный полимер, включающий другие различные олигомерные системы (HNIPU). Значительное внимание было уделено материалам на основе возобновляемых необработанных источников. Автор приводит обзор последних публикаций в данной области с более подробным описанием достижений Polymate Ltd.

**Ключевые слова:** неизоцианатные полиуретаны, циклические карбонаты, полигидроксиуретановый полимер.

## **INTRODUCTION**

Polyurethanes (PU) are among the most sought-polymers in the many of modern technologies [1].

However, the involvement of toxic components, such as isocyanates, in the fabrication process renders PU production extremely toxic and dangerous [2].

In the field of PU preparation for a long time are being sought nonisocyanate sources of polyurethanes. Nonisocyanate polyurethanes (NIPU) on the base of polycyclic carbonates and polyamines are known for more than 50 years. Fundamentals of the practical application of NIPU in coatings, sealants, adhesives, etc. were developed in detail by O. Figovsky in the 70-80's [3-14]. Recently some reviews devoted to synthesis of cyclic carbonates and NIPU were presented [15–17]. In these works the positives of NIPU were described in detail.

NIPU networks are obtained by reaction between the polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups [15]. This forms a crosslinked polymer with  $\beta$ -hydroxyurethane groups of different structure – polyhydroxyurethane polymer. Since NIPU is obtained without using of



highly toxic isocyanates, the process of synthesis is a fairly reliable in terms of safety and environmental impact – in contrast to conventional polyurethanes. The model scheme of the two options  $\beta$ -hydroxyurethane fragments of polymer chains formed in the case of diffunctional starting materials is shown in Figure 1.



Figure 1.  $\beta$ -hydroxyurethane moieties of nonisocyanate polyurethanes: A – with secondary hydroxyl groups; B – with primary hydroxyl groups

Moreover, NIPU is not sensitive to moisture in the surrounding environment. Formed hydroxyl groups at the  $\beta$ -carbon atom of the urethane moiety promote adhesion properties. Plurality of intra- and intermolecular hydrogen bonds [18, 19] as well as no contamination of unstable biuret and allophanate units [20] seems to be responsible for increasing of thermal stability and chemical resistance to non-polar solvents.

However, for more than 50 years since the first publication in this field, NIPU still do not have a sufficiently broad application. This can be explained by certain features of these materials. Cyclic carbonate (CC) groups interact with aliphatic and cycloaliphatic polyamines at ambient temperatures slower than isocyanates with hydroxyl groups. The rate of this reaction is comparable to the rate of curing epoxy resins (ER) with amines. At the same time, the CC react only with primary



amino groups, in contrast to the ER, which react with primary and with secondary. This results in a decrease in crosslinking density of the polymer network.

#### **BRIEF DESCRIPTION OF RECENT WORKS IN THE FIELD OF NIPU**

Great problem of the NIPU technologies is the practically absence of commercially available multifunctional cyclic carbonates. Recent work in the field of new methods for preparing of cyclic carbonates devoted primarily to the development of new catalytic systems and the synthesis of monofunctional compounds (see for example reviews [21, 22]). Similar catalyst systems are used also for the copolymerization of epoxides and CO<sub>2</sub> and ring-opening polymerization of cyclic carbonates [23, 24], and one or the other direction of the reaction depends on the process conditions. Preparative synthesis of mono- and polycyclic carbonates for research purposes are provided by the company Specific Polymers, France [25].

Bernard (Rhodia) propose a method for preparing polyhydroxy-urethanes, said method comprising reacting 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 [26]. An object of this invention is to propose predominantly aqueous formulations on the base of polyfunctionalized polyhydroxy-urethane intermediates, as well as a method for preparing said formulations and their uses, especially for producing coatings, adhesives, and others. However, the described process is very complicated and time-consuming, requires large amounts of organic solvents, and formulations for 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 [27]. But in this case also component (A) comprises a reaction product of hydroxyl group-containing cyclic carbonate with an isocyanate group-containing polyurethane prepolymer.

Currently in the coatings industry cyclic carbonate raw materials often suggest to use in hybrid epoxy-hydroxyurethane compositions [16]. Use of such systems assumes preliminary receiving of the adducts of the cyclic carbonates and amines. These adducts (also named as aminourethanes) 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.) [27a] describes a curable composition comprising: 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 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 [27b].

Also researches of Huntsman Co. proposed filled compositions on the base of NIPU or HNIPU and nano-clays [28-31]. In this work were used some of synthesized in Polymate Ltd. cyclic carbonates (as row materials).

Klopsch et al. (BASF) disclose the use of new cyclic carbonates with unsaturated bonds as reactive diluents in epoxy resin compositions [32]. It has been found that the addition just of 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 presented.

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 [33].

The problem of obtaining NIPU materials based on renewable raw materials is given considerable attention in the research centers of the U.S. (Wilkes and coworkers, Doll, Erhan, Holser, Javni, Petrović et al.), in Poland (Rokicki and coworkers) and China (Kang, Li et al.) [16].

Recently, a number of European academic centers have begun to actively develop direction of NIPU from plant-based raw materials. Thus, researchers at the Institute of Macromolecular Chemistry at the University of Freiburg investigate soy- and linseed oil-based polyurethanes prepared by curing carbonated soybean (CSBO) and linseed (CLSO) oils with different diamines. Later thay have reported on a very versatile new route to linear as well as cross-linked terpene-based nonisocyanate poly(hydroxyurethanes) (NIPU) and prepolymers derived from the novel cyclic limonene dicarbonate (CL) [34,35]. The catalytic carbonation of epoxidized limonene with CO<sub>2</sub> was monitored in the presence of both homogeneous tetrabutylammonium bromide (TBAB) and heterogeneous silica supported 4-pyrrolidinopyridinium iodide (SiO<sub>2</sub>-(I)) catalysts. The systematic variation of catalyst type,  $CO_2$  pressure and temperature enabled quantitative carbonation in bulk and incorporation of 34.4 wt.% CO<sub>2</sub> into CL. In contrast to conventional plant-oil-based cyclic carbonates, such terpene-based cyclic carbonates afford much higher CO<sub>2</sub> fixation and do not contain ester groups. The absence of ester groups is essential to prevent side reaction during amine cure such as ester cleavage and amide formation, impairing network formation and causing emission of low molecular weight polyols which can plastify NIPU. Novel linear



NIPU und 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 (epoxidized compounds) were obtained in two material steps by а transesterification is conducted starting from a monoalkyl esters of unsaturated acids and a diols, and subsequent epoxidation. Then the biscarbonates were prepared from difunctional epoxides and supercritical CO<sub>2</sub> in the presence of ionic liquids and tetrabutylammonium bromide (TBABr) as the catalyst. Received cyclic carbonates were considered as polyhydroxyurethane precursors and further selfpolycondensed with ethylene diamine and isophorone diamine to form polyurethanes [36-39]. For preparation of bicarbonates with terminal cyclic carbonate groups were used metathesis reaction with Hoveyda's catalyst.

Researches from Reutlingen University and 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 carbon dioxide 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 [40].

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  $150^{\circ}$  C for 9 h under vacuum to produce high molecular weight polymers [41]. Although the polymers are produced at a high temperature above properties still do not allow them to find a practical application.

It is continues development of the direction of silicon-contained and nanostructured hydroxyurethane compounds (see our previous rewiev [16]). Turkish researchers synthesized a novel carbonate-modified bis(4-glycidyloxy phenyl) phenyl phosphine oxide (CBGPPO) for preparing of nonisocyanate 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 [42].

A novel bis-urethane organosilane precursor has been developed via NIPU route in sol-gel processing conditions and employed as an organic precursor of organicinorganic 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 [43].

Hanada et al. disclose a polysiloxane-modified polyhydroxy polyurethane resin being derived from a reaction between a 5-membered cyclic carbonate polysiloxane compound (Figure 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 [44].



Figure 2. Example of five-membered cyclic carbonate polysiloxane compound

#### **RECENT ACHIVEMENTS OF POLYMATE LTD**

#### Polyhydroxyurethanes

Usually polyhydroxyurethane polymer is not enough water resistant due to plurality of hydroxyl groups. But it is possible to prepare water resistant materials in some formulations. For example, on the base of acrylic epoxy oligomers was prepared cyclocarbonate acrylic polymers with high water and weather stabilities. It was elaborated paint with curing temperature 110°C, 2-3 hour. Unfortunately we need to use solvents for this composition [15].

Recently, the company Polymate works on the synthesis of aliphatic multifunctional cyclic carbonates from corresponding epoxies and carbon dioxide and NIPU based on them. Authors tested some compositions of synthesized in the laboratory polyfunctional carbonates, namely trimethylol propanetricyclocarbonate (TMPTCC) and chlorine-contained aliphatic tricyclocarbonates (on the base of chlorine-contained aliphatic epoxy resins Oxilin<sup>TM</sup>) 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.<sup>TM</sup> 20, Dow Chemical Co..

Properties of these materials are shown in Table 1.



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

Table 1

Some of the results significantly higher than previously achieved level and offer good prospects for their practical use. Further elaboration will be provided.

#### Hybrid nonisocyanate polyurethanes

Recently authors proposed compositions based on oligomer systems which contain a hydroxy-amine adducts on the base of aliphatic mono- and polycyclic carbonates (Cycloate  $A^{TM}$ ) as hardeners [45]. This compositions used for 100 % solid floorings and have high abrasion resistance and mechanical properties. Thus in the Polymate were elaborated practically used formulations on the base of HNIPU, for example F1 and F2 (Table 2).

#### Hydroxyurethane modifiers (HUM)

A separate area of the NIPU-technology is use of the pure hydroxyalkyl urethane compounds. Now all known polymer compositions with hydroxyalkyl urethane monomers demand specific chemical reactions (such as transetherification, transamination, or self-cross-linking). These reactions are carried out at elevated temperatures, in the presence of organic solvents, and/or in water-dispersion media, sometimes in the presence of catalysts [16].

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Composition	Parts by weight		
Composition	F1	F2	
Hydroxyl-amine adduct "1" (on the base of Cycloate A <sup>TM</sup> )	50.0	-	
Hydroxyl-amine adduct "2" (on the base of Cycloate A <sup>TM</sup> )	-	50.0	
Epoxy resin D.E.R.® 324 of Dow chemical	45.0	40.0	
Polycyclic carbonate Cycloate A <sup>TM</sup>	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, hr	4	6	
After 7 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, 1000 cycles/1000 g, CS-17 wheel, mg	27	29	
Impact resistance, N·m, $\geq$	20	20	

Table 2. Composition and Properties of Flooring Compounds

Recently the authors proposed novel concept of generating new multifunctional modifiers. The HUM, which possesses a wide range of hydrogen bonds, embedded in epoxy polymer network without a direct chemical interaction.



In our patent application [46] were disclosed a novel "cold" cure epoxy-amine compositions modified with a hydroxyalkyl urethane (HUM), which is obtained as a result of a reaction between a primary amine ( $C_1$ ) and a monocyclocarbonate ( $C_2$ ), wherein modifier (C) is represented by the formula in Figure 3:



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

wherein  $R^1$  is a residue of the primary amine,  $R^2$  and  $R^3$  are the same or different and are selected from the group consisting of H, alkyl, hydroxyalkyl, and n satisfies the following condition:  $n \ge 2$ . Diluents, pigments and additives can be used. The influence of the new modifier primarily affects a significant acceleration of the curing process, as well as non-trivial increase in abrasion resistance. Doping with the HUM impart 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, are not worse.

Dependences of curing characteristic and abrasion resistance from content of HUM-01 are shown on Figure 4 [47].

The following sections will be given at examples of successful application of HUM for other oligomeric systems.

## Hydroxyurethane compounds from renewable plant-based raw materials

Recently authors propose a new method of producing a hybrid polyhydroxyurethane network comprising [48]:



Figure 4. Influence of modifier HUM-01 (trimetyl-hexametylene-diamine + propylene carbonate)

on the properties of epoxy composition based on D.E.R. 331

(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 oxyrane 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); (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: (i) a compound having epoxy functionality, and (ii) 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 the time of synthesis and improve the quality of the final products.



Figure 5. Obtaining of carbonated-epoxidized unsaturated fatty acid triglycerides

#### Silicon-contained 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 carbonateepoxy resin systems and aminoalkoxysilanes [49]. The proposed dendroaminosilane 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 nanostructured network polymer.



Known in the art 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 [16].

A novel nanostructured hybrid polymer compositions were 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 [50]. The composition is highly curable at low temperatures (approximately 10 to 30° C.) with generating of nanostructure (Figure 5) under the influence of the forming of active, specific hydroxyl groups by reaction of cyclic carbonates with amine functionalities. These hydroxyurethane functionalities activate of 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 has excellent strength-stress properties, adhesion to a variety of substrates, appearance, and resistance to weathering, abrasion, and solvents.

#### **Sprayable Foam**

A basic composition and a technique for mixing and foaming were developed for insulating foam applied by spraying, the material being based on the use of the synthetic raw materials. A standardized procedure for obtaining polyurethane foams was approved. Technical specifications of this newly developed composition correspond to 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 pores). Possibility of application by spraying was tested on simulating equipment.



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

Recently the composition of the foam was studied by the use of renewable raw materials, including new HUM. As a result, hard and elastic foams were obtained with propertied not inferior to polyurethane foams. The foams were produced in the laboratory only (Table 3).

Development of new foams is expedient and can be continued.

#### 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 provide a durable, high-performance and eco-friendly solution. These thin-film coating systems cure instantly, thereby minimizing the downtime of any facility. Other benefits of these coatings include excellent chemical resistance, easy clean ability, little odor, and the ability to coat in cold conditions.



#### Table 3. Rigid HNIPU foam

PROPERTIES	STANDARD	Rigid Foam
		Insulation
Viscosity (Brookfield RVDV II, Spindle	ASTM D2393	
29, 20 rpm) at 25°C, cP		
Base "A"		2800 - 3200
Base "B"		3600-4100
"A" + "B" (3-5 sec after mixing)		≤3700
Pot life at: 25°C (77 °F), s		8-10
VOC	ASTM D2369	Compliant
Gel time, s		2-4
Touch dry, s		30-40
Curing for transportation, min		15-20
Appearance of rigid foam		White
<b>Compressive Properties of Rigid</b>	ASTM D 1621	
Cellular Plastics,		0.02 - 0.04
24 hours, $kgf/mm^2$		
Apparent Density of Rigid Cellular	ASTM D2794	30-40
Plastics, Kg/m <sup>3</sup>		
Thermal Transmission Properties by Means		
of the Heat Flow Meter Apparatus, hr.ft <sup>20</sup> F	C 518	4.5-5.0
/Btu.in		

The surface preparation and applying 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 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 and 0.8 mm.

Unlike conventional UV-curable coating, formulations developed by our company contain up to 60% of vegetable oils derivatives, such as modified soybean oil. This allows obtaining a composition of higher elasticity while maintaining the basic strength characteristics. The use of our compounds improves the adhesion of the cured composition to concrete, allows reducing 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 our new hydroxyurethane modifier (HUM) based on vegetable raw materials, and adducts obtained on its basis, allow improving hardness and wearing resistance, while maintaining the other properties of the system (Table 4).

The uniqueness of the developed formulation and the possibility of coating concrete sometimes without a primer, with layer thickness of 0.3-0.8 mm allow 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.



# Table 4. Properties of HNIPU UV-cured flooring compared to conventional UVcured flooring

Properties	Standard	Conventional UV-	HNIPU UV-cured
		cured flooring	flooring
Adhesion	ASTM D 3359-07,	3B	5B
	В		
Pencil hardness	ASTM D 3363-05	3Н	4H
Solvent resistance	ASTM D5402-06	200+	200+
Gloss	ASTM D 523	84	90
Abrasion resistance, CS-	ASTM D1044	150-200	100
17, 1000 grams, 1000			
cycles, mg			
Thickness applied, mm		0.065-0.1	0.3-0.8
Primer		Required	Not required for
			properly prepared
			substrates
No. of layers		2+	1

## CONCLUSIONS

Many well-known companies and research centers in the world intensive develop new methods for the synthesis of cyclic carbonates and compositions thereof. Leading positions in the development of non-isocyanate materials held research center Polymate Ltd.

For further developments in the field of polyhydroxyurethanes, we believe themost appropriate the following directions:

1. Creation of production of polyfunctional cyclocarbonates, development of optimal technology and equipment:

- carbonized vegetable oils and terpenes;



- carbonized aliphatic compounds, including chlorinated ones;
- carbonized polyfunctional silicones.
- 2. Development of waterborne HNIPU formulations.
- 3. Development of NIPU formulations for sealants and adhesives.
- 4. Development of production of amines modified with hydroxyurethane groups.
- 5. Elaboration of non-amine RT curing agents for oligomer compositions.
- 6. Development of self-extinguishing compositions of HNIPU.
- 7. Development of silicone-based HNIPU.
- 8. Development of NIPU and HNIPU-based foams.
- 9. Development of formulations for UV-cured compositions.

# 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, Hannover, 2007, 344 p.

- 3. Figovsky O. Soviet Union patents: SU529197, 1976.
- 4. Figovsky O. Soviet Union patents: SU563396, 1977.
- 5. Figovsky O. Soviet Union patents: SU628125, 1978.
- 6. Figovsky O. Soviet Union patents: SU630275, 1978.
- 7. Figovsky O. Soviet Union patents: SU659588, 1979.
- 8. Figovsky O. Soviet Union patents: SU671318, 1984.
- 9. Figovsky O. Soviet Union patents: SU707258, 1984.
- 10. Figovsky O. Soviet Union patents: SU903340, 1982.
- 11. Figovsky O. Soviet Union patents: SU908769, 1982.
- 12. Figovsky O. Soviet Union patents: SU1126569, 1984.
- 13. Figovsky O. Soviet Union patents: SU 1754747, 1992.
- 14. Figovsky O. Soviet Union patents: SU 1754748, 1992.



15. 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. N.Y., Taylor & Francis, 2006.

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

17. Guan J., Song Y., Lin Y., Yin X., Zuo M., Zhao Y., Tao X. and Zheng Q."Progress in Study of Non-isocyanate Polyurethane", Ind. Eng. Chem. Res. 2011, 50, 6517-6527.

18. 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.

19. 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.

20. Tomita H., Sanda F. and 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.

21. North M., Pasquale R. and Young C. Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. *Green Chem.*, 2010, 12, 9, 1514-1539.

22. Pescarmona P.P., Taherimehr M. Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO<sub>2</sub>. *Catal. Sci. Technol.*, 2012, 2 (11), 2169-2187.

23. Kember M.R., Buchard A. and Williams C.K. Catalysts for CO<sub>2</sub>/epoxide copolymerization. *Chem. Commun.*, 2011, 47, 1, 141-163.



24. Guillaume S.M. and Carpentier J-F. Recent advances in metallo/organo-

catalyzed immortal ring-opening polymerization of cyclic carbonates. *Catal. Sci. Technol.*, 2012, **2**, 898–906.

25. Carbonates for non-isocyanate polyurethane.

URL:specificpolymers.fr/medias/downloads/nipur.pdf

26. Bernard J.-M. Method for preparing polyhydroxy-urethanes. US Patent 8,

017,719, 2011; US Patent Application 2011/0288230, 2011.

27. Moeller T., Kinzelmann H.-G. Two-component bonding agent. US Patent 8, 118, 968, 2012.

27 (a). Muller-Frischinger I. Coating system. US Patent 8,003,737, 2011; (b) Muller-Frischinger I.,

27 (b). Gianini M., Volle J. Coating system. US Patent 8,263,687, 2012.

 Diakoumakos C.D., Kotzev D.L. Nanocomposites based on polyurethane or polyurethane-epoxy hybrid resins prepared avoiding isocyanates. US Patent 8, 2012.

29. Diakoumakos C.D., Kotzev D.L. US Patent 143, 2012.

30. Diakoumakos C.D., Kotzev D.L. US Patent 346, 2012.

31. Diakoumakos C.D., Kotzev D. L. Non-Isocyanate-Based Polyurethane and Hybrid Polyurethane-Epoxy Nanocomposite Polymer Compositions. US Patent Application 2012/0149842, 2012.

32. Klopsch R., Lanver A., Kaffee A., Ebel K., Yu M. Use of cyclic carbonates in epoxy resin compositions. US Patent Application 20110306702, 2011.

33. 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.

34. 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;



35.Bähr M., Bitto A. and 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.

36. Cramail H., Boyer A., Cloutet E., Gadenne B., Alfos C. Bicarbonate precurors, method for preparing same and uses thereof. WO 2011061452, 2011 and US Patent Application 2012/0259087, 2012.

37. Foltran S., Maisonneuve L., Cloutet E., Gadenne B., Alfos C., Tassaing T., Cramail H. Solubility in  $CO_2$  and swelling studies by *in situ* IR spectroscopy of vegetable-based epoxidized oils as polyurethane precursors. Polym. Chem., 2012, 3 (2), 525-532.

38. Foltran S., Maisonneuve L., Cloutet E., Cramail H., Gadenne B., Alfos C., Tassaing T. An efficient in-situ FTIR method for the determination of the thermodynamic properties of carbon dioxide/liquid mixtures. 10th International Symposium on Supercritical Fluids (ISSF 2012), San Francisco, CA, USA, 13-16 May 2012. P-0902.

39.Foltran S., Alsarraf J., Robert F., Landais Y., Cloutet E., Cramail H., Mereau R., Tassaing T. On the Chemical Fixation of Supercritical Carbon Dioxide with Epoxides Catalyzed by Ionic Liquids: a Combined Spectroscopic and Computational Study. 10th International Symposium on Supercritical Fluids (ISSF 2012), San Francisco, CA, USA, 13-16 May 2012. P-1602.

40. Mahendran A.R., Aust N., Wuzella G., Müller U. and Kandelbauer A. Biobased non-isocyanate urethane derived from plant oil. J. Polymers and the Environment, 2012.

41. 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.

42. Hoşgör Z., Kayaman-Apohan N., Karataş S., Menceloğlu 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, P. 366–375.

43. 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.

44. Hanada K., Kimura K., Takahashi K., Kawakami O., Uruno M. Fivemembered cyclic carbonate polysiloxane compound. Polysiloxane-modified polyhydroxy polyurethane resin. US Patent Applications: 20120231184, 20120232289 and 20120237701, 2012.

45. 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.

46. Birukov O., Figovsky O., Leykin A., Shapovalov L. Epoxy-amine composition modified with hydroxyalkyl urethane. US Pat. 7989553 B2, 2011.

47. Figovsky O., Birukov O., Shapovalov L., Leykin A. Hydroxyurethane modifier as effective additive for epoxy matrix. Scientific Israel – Technological Advantages 2011, 13 (4), 122-128.

48. 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

49. Figovsky O., Shapovalov L., Buslov F. Ultraviolet and thermostable nonisocyanate poly-urethane coatings. Surface Coatings International Part B: Coatings Transactions, 2005, 88 (B1), 67-71.

50. Birukov O., Beilin D., Figovsky O., Leykin A., Shapovalov L. Nanostuctured hybrid oligomer composition. US Pat. 7,820, 779 B2, 2010.