Nanostructured Composites based on Interpenetrated Polymer Networks

Nonisocyanate Polyurethanes based on Cyclic Carbonates and Nanostructured Composites

Part I

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Abstract: Recent advances in chemistry and technology of nonisocyanate 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 composites comprising of silanes are also considered. An overview of the recent publications in this field is provided with a more detailed description of achievements by the authors and their corporate employees. The use of NIPU materials as coatings, adhesives, and foams is described.

Key words: nonisocyanate polyurethanes, cyclic carbonate oligomers, hybrid polymers

Introduction

NIPU networks are obtained by the reaction between polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups [1-5]. This forms a cross linked polymer with ***p***-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 bifunction-al starting materials is shown in Fig.1**.**

Moreover, NIPU is not sensitive to moisture in the surrounding environment. Hydroxyl groups formed at the ***p***-carbon atom of the urethane moiety also increase adhesion properties. Plurality of intra- and intermolecular hydrogen bonds [6, 7] as well as the absence of unstable biuret and allophanate units [8] seems to be responsible for increased thermal stability and chemical resistance to non-polar solvents.

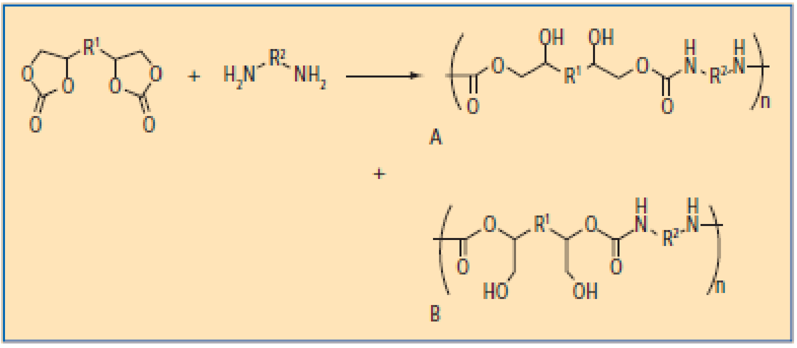

Fig.1. ***β***-hydroxyurethane moieties of non-isocyanate poly-urethanes: **A** - with secondary hydroxyl groups; **B** - with primary hydroxyl groups [3]

The mechanism of the reaction of cyclic carbonates with amines, providing nonisocyanate 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 [9, 10]. 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 [1, 6, and 7]. 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.

State of the Art in NIPU:
Brief Description of the Latest Discoveries and Developments

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 [11, 12]. Similar catalyst systems are used also for the copolymerization of epoxies and CO_2 and ring-opening polymerization of cyclic carbonates [13, 14], 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 [15].

Bernard [16] proposes a method for preparing polyhydroxyurethanes, which comprises of reacting of:

- at least *one compound* having a cyclic carbonate functional group and at least one hydroxyl functional group;
- at least *one compound* having at least one linear carbonate functional group;
- at least *one compound* having at least one primary or secondary amine functional group.

The subject of this invention is to position predominantly aqueous formulations on the base of polyfunctionalized polyhydroxyurethane intermediates, as well ascreating 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. [17] 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. In this case also component (A) comprises of the reaction product of hydroxyl group-containing cyclic carbonate with an isocyanate group-containing polyurethane prepolymer. Currently in the coatings industry cyclic carbonate raw materials are often suggested for the use in hybrid epoxy-hydroxyurethane compositions [18]. 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 [19] describes a curable composition comprising of:

a. Mixture of an epoxy resin a cyclic carbonate
b. Curing agent - hybrid hardener, whereby said hardener is a blend of:
    - an aminic compound, and
    - Adicyclopentadiene-phenol based Novolac.

Later Muller-Frischinger et al. [20] disclosed 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. Also researches of Huntsman Co. [21] proposed filled compositions on the base of NIPU or HNIPU and nanoclays. In this work cyclic carbonates, synthesized by Polymate Ltd.-INRC, were used as raw materials.

Klopsch et al. [22] disclose the use of new cyclic carbonates with unsaturated bonds as reactive diluents in epoxy resin compositions. 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. [23] proposed 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. The problem of obtaining NIPU materials based on renewable raw materials is given considerable attention in the research centers of the USA, Europe and China [18].

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 curingcarbonated soybean (CSBO) and linseed (CLSO) oils with different di-amines [24]. Later they have reported on a very versatile new route to linear as well as cross linked 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 CO_2 was monitored in the presence of both homogeneous tetrabutylammonium bromide (TBAB) and heterogeneous silica supported 4-pyrrolidinopyridinium iodide (SiO_2-(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_2 into CL. In contrast to conventional plant oil-based cyclic carbonates, such terpene-based cyclic carbonates afford much higher CO_2 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 byproducts 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. [26] reported polyaddition of diamines with vegetable-based biscarbonates to prepare new polyurethanes. The intermediate materials (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 CO_2 in the presence of ionic liquids and TBAB as the catalyst. Received cyclic carbonates were considered as polyhydroxyurethane precursors and further self-polycondensed with ethylene diamine and isophorone diamine to form polyurethanes. For preparation of bis-carbonates with terminal cyclic carbonate groups were used in a metathesis reaction with Hoveyda's catalyst.

The article [27] presents 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 CO_2 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.

A novel bio-based, isocyanate-free poly-(amide urethane) derived from soy dimer acids is described in [28]. 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. 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 nanostructured hydroxyurethane compounds. HoşgörZ.,et al. [29] synthesized a novel carbonate-modified bis(4-glycidyloxy phenyl) phenyl phosphine oxide (CBGPPO) for preparing 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.

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. [31] disclosed a polysiloxane-modified polyhydroxy polyurethane resin being derived from a reaction between a five-membered cyclic carbonate polysiloxane compound and an amine compound, its production process and a resin composition (Fig.2).

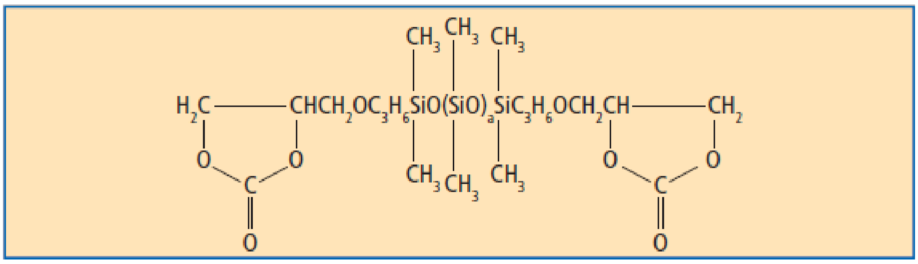

Fig.2. Example of five-membered cyclic carbonate polysiloxane compound [3]

New materials can be used for thermal recording medium, imitation leather, thermoplastic polyolefin resin skin material, weather strip material, and weather strip.

Recent Achievements in the Feld of HNIPU

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 [1].

Researches on the synthesis of aliphatic multifunctional cyclic carbonates from corresponding epoxies and carbon dioxide and NIPU based on them were carried out. Some compositions of polyfunctional carbonates synthesized in the laboratory were examined, namely: trimethylolpropane tricyclocarbonate (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.

Table 1

Properties of the polyhydroxy urethanes [3]

Cyclocarbonate	Amine	Tensile strength, MPa	Elongation %	Water absorption %
TCCTMP	MPDM	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

One can see that some results are significantly higher than previously achieved levels and offer good prospects for their practical use.

Hybrid Non-Isocyanate Polyurethanes (HNIPU)

Recently the authors and their corporative employees proposed compositions based on oligomer systems which contain hydroxylamine 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, we have developed practically used formulations on the basis of HNIPU, using the two formulations F1 and F2 shown in Table 2.HNIPU Flooring and paint application is shown in Table 3a,b

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Table 2

Composition and properties of flooring compounds [3]

Composition	Parts by weight	
	F1	F2
1	2	3
Hydroxyl-amine adduct "1" (on the base of Cycloate A)	50.0	-
Hydroxyl-amine adduct "2" (on the base of Cycloate A)	-	50.0

1	2	3
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

Table 3a.

HNIPU Flooring Application: Indoor/Outdoor for Industrial & Commercial Buildings; Garages; Chemical Plants; Warehouses; Monolithic Flooring for Civil, Industrial and Military Engineering, Marine Apps, etc.

Product Name	Specific Properties
1	2
FLI4W	Increased chemical, wearing, light and humidity resistance plus high sanitary-hygienic properties. Application temperature: 50-68 ˚F (10-20 ˚C)
FLI4W-FC	Same as FLI4W but shorter curing time and pot life (10-30 min)
FLI4W-LP	Same as FLI4W but longer pot life (2-3 hours)
FLI4W-B	Same as FLI4W but longer pot life (up to 4 hours)

1	2
FLIO6W	Higher light resistance. Application temperature: 50-68 ˚F (10-20 ˚C)
FLIO6S	Same as FLIO6W but increased "ultra" UV resistance
FLI3	Low application temperature: 36-77 ˚F (2-25 ˚C), fast curing, high sanitary-hygienic properties

Table 3b.

HNIPU Paint Application:Indoor/Outdoor for Industrial & Commercial Buildings; Chemical Plants; Marine Apps; Protective Coatings Inside Pipes; Equipment for Liquid Fertilizer Delivery; Military Equip., etc.

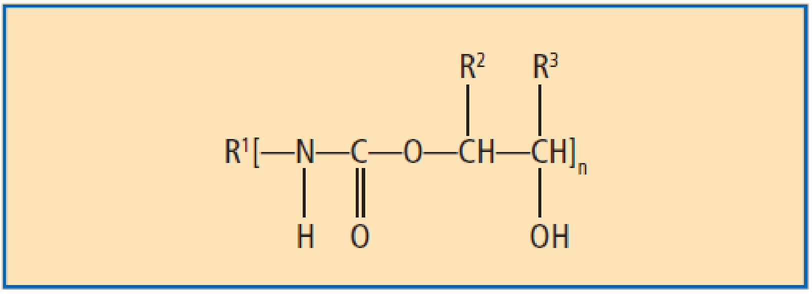
Product Name	Specific Properties
PI9W	Paint for indoor light stable and chemical resistant applications. Application temperature: 50-68 ˚F (10-20 ˚C)
PIO15W	Increased light resistance and high decorative properties. Application temperature: 50-68 ˚F (10-20 ˚C)
PIO15S	Same as PIO15W but increased "ultra" UV resistance

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 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 [18]. 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

Patent [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 Fig.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 > 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.



$$R^1\Big[-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-O-\overset{\displaystyle R^2}{\overset{|}{CH}}-\overset{\displaystyle R^3}{\overset{|}{\underset{\underset{\displaystyle OH}{|}}{CH}}}\Big]_n$$

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

Two advanced curing agents were elaborated: Uramine 5851 (on the base of HUM-01) and Uramine 4761 (on the base of HUM-14).Table 4illustrated comparative properties of Uramines and conventional amine hardeners. Comparison Uramine 5851 with Vestamin TMD and Ancamin 2379 was carried out using epoxy resin D.E.R. 331. Comparison Uramine 4761 and Vestamin IPD was carried out using hydrogenated epoxy resin ST-3000.

As seen from Table 4 Uramines accelerate the curing of epoxy composites, improve the appearance of coatings, and reduce abrasive wear. Uramines virtually no effect on the strength and elasticity, and also on the chemical resistance of the polymer.

Table 4.

Comparative properties of Uramines and conventional amines

Technical Data	Sample 1 DER 331 + TMD	Sample 2 DER 331 +Ancamine 2379	Sample 3 DER 331 + Uramine 5851	Sample 4 ST-3000 + IPD	Sample 5 ST-3000 +Uramine 4761
Ratio: **A** (DER-331)**:** **B** (Curing agent**)**	100:21	100:46	100:55	100:19	100:25
Pot life, min	45	20	10	240	60
Gel Time, min	65	30	20	360	120
Dry to touch, h	>20	>2	1.5	8	3.5
Shore D 25ºC 24h	79	75	75	70	70
Shore D Full Cure	82	80	81	80	78
Tensile strength kg/mm^2	6.4	5.8	6.6	5.5	4.7
Ultimate Elongation, %	3.1	4.4	4.8	4.4	5
Abrasion, Taber, loss of mass, mg /1000 cycles	57	36	20	58	31
Weight gain at immersion in water (24 h @ 25ºC), %	0.1	0.3	0.2	0.2	0.3
Weight gain at immersion in 20% H_2SO_4	0.7	0.5	0.4	1.2	1.2
Weight gain at immersion in 20% NaOH	0.4	0.2	0.2	0.1	0.1
Appearance	Sticky 24h, semi gloss	gloss	gloss	mat surface	gloss

The dependences of curing characteristic and abrasion resistance from content of HUM-01 are shown in Fig.4 [3, 34]. The following sections provide examples of successful applications of HUM into other oligomeric systems

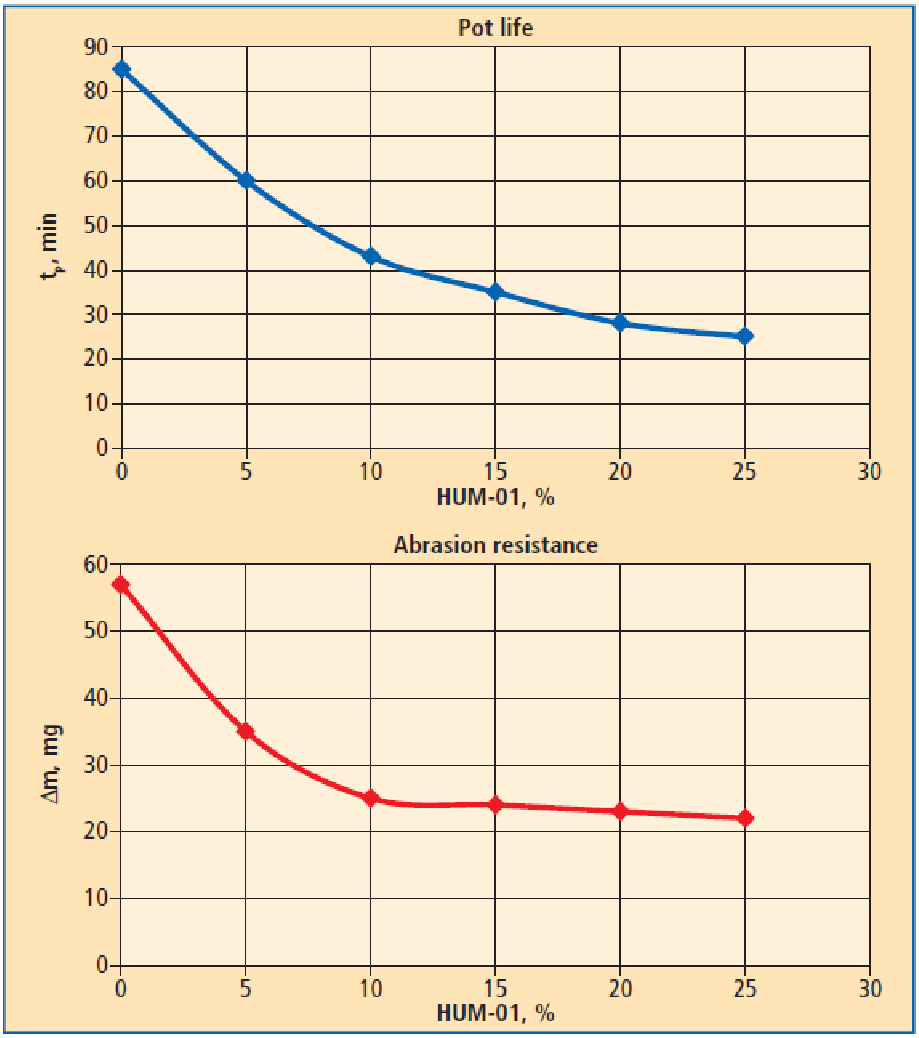


Fig.4. Influence of modifier HUM-01 (trimetyl-hexametylene-diamine + propylene carbonate) on the properties of epoxy composition based on D.E.R. 331 [3, 34]

Summing up we can say that:

Uramine 4761 and Uramine 5851 are hardeners for epoxy base compositions of novel type. Due to presence of hydroxyurethane modifiers the Uramines impart to cured compositions the best properties of epoxy and urethane coating materials. Created on the nonisocyanate base Uramines don’t have the toxicity of conventional urethanes.

Uramines aimed for receiving wide range of coating materials (clear or colored, filled floorings, paints, etc.) with needed properties depending of base used, in particular:

- Low VOC, 100 % solid;
- Waterbased;
- High abrasion resistant (20-30 mg at 1000 cycles, 1000 g, CS-17, ASTM D4060);
- High weather resistant (at least 3000 hours, UVA, ASTM G154);
- Improved chemical resistance, flexibility, impact resistance, adhesion to substrates, etc.;
- Uramines provide fast curing (at 25o C.: gel time 20-60 min; thin film set time 1.5-2.0 hours), but if needed gel time may be prolonged to 4 hours.
- Excellent appearance.

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 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 us 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 (Table 5).

Table 5

Properties of HNIPU UV-cured flooring
compared to conventional UV-cured flooring

Properties	Standard	Conventional UV-cured flooring	HNIPU UV-cured flooring
1	2	3	4
Adhesion	ASTM D 3359-07, B	3B	5B
Pencil hardness	ASTM D 3363-05	3H	
Solvent resistance	ASTM D 5402-06	200+	4H
Gloss	ASTM D 523	84	90
Abrasion resistance, CS-17, 1,000 g, 1,000 cycles, mg	ASTM D 1044	150-200	100

1	2	3	4
Thickness applied, mm		0.065-0.1	03-0.8
Primer		Required	Not required for properly prepared substrates
Number of layers		2+	1

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.

To be continued

References

1. Figovsky O., Shapovalov L. Cyclocarbonate Based Polymers Including Non-Isocyanate Polyurethane Adhesives and Coatings. Encyclopedia of Surface and Colloid Science, V. 3, 1633 – 1653. NY, Taylor & Francis, 2006.
2. Figovsky O., Beilin D. Advanced Polyner Concretes and Compounds, CRC press, Taylor& Francis, 2014.
3. Figovsky O., Shapovalov L., Leykuin A., Birukova O., Potashnikiova R. Recent Advances in the Development of Nonisocyanate Polyurethanes Based on Cyclic Carbonates, PU Magazine, vol.10, no.4, 2013, pp. 256-263.
4. Figovsky O., Beilin D. Nanostructured Composites Based on Interpenetyrated Polymer Networks: Kinds, Classification, Properties, Synthesis, Application. Inženernyj vestnik Dona (Rus), 2015, no.3, (Accepted for publication). Url: ivdon.ru/ru/magazine/archive/n3y2015/.
5. Figovsky O., Shapovalov L., Leykin A., Birukova O., Potashnikova R. Progress in Elaboration of Nonisocyanate Polyurethanes Based on Cyclic Carbonates. Inženernyj vestnik Dona (Rus), 2014, no.3. Url: ivdon.ru/ru/magazine/archive/n3y2014/2530.
6. Figovsky O., Shapovalov L., Leykin A.,Beilin D.. Nanostructured Hybrid Nonisocyanate Polyurethane Coatings, Proceeding of PPS Americas Conference, Niagara Falls, Ontario, Canada, May 21-24, 2012, pp.396-397.

7. 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.
8. 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.
9. 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.
10. 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.
11. North M., Pasquale R., Young C., Synthesis of Cyclic Carbonates from Epoxides and CO_2.Green Chem., 2010, 12, 9, 1514 – 1539.
12. Pescarmona P. P., Taherimehr M., Challenges in The Catalytic Synthesis of Cyclic and Polymeric Carbonates from Epoxides and CO_2.Catal. Sci. Technol., 2012, 2 (11), 2169 – 2187.
13. Kember M. R., Buchard A., Williams C. K., Catalysts for CO_2/Epoxide Copolymerization. Chem. Commun., 2011, 47, 1, 141 – 163.
14. 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.
15. Url: specifi cpolymers.fr/medias/downloads/nipur.pdf.
16. Bernard J.-M. Method for Preparing Polyhydroxy-Urethanes. US Patent 8,017,719, 2011; US Patent Application 2011/0288230, 2011.
17. Moeller T., Kinzelmann H.-G. Two Component Bonding Agent. US Patent 8,118,968, 2012.
18. 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.
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; 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 Composition. 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., MülhauptR.,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 precurors, 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 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.
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(Amideurethane)s via Non-Isocyanate Route. PU Magazine International, 2012,9 (4), 255 – 257.
29. Hoşgör Z., Kayaman-Apohan N.,Karataş S., Mencelocğlu 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., ShapovalovL.,Leykin A., Hydroxyurethane Modifier as Effective Additive for Epoxy Matrix. Scientific Israel – Technological Advantages 2011, 13 (4), 122 – 128.
35. Rokickia G., Parzuchowski P.G., Mazureka. Nonisocyanate Polyurethanes: Synthesis, Properties, and Applications. Polym. Adv. Technol. 2015, no.26 pp.707–761.
36. Birukov O., Figovsky O., Leykin A., Potashnikov R., Shapovalov L. , Method of Producing Hybrid Polyhydroxyurethane Network on a Base of Carbonatedepoxidized Unsaturated Fatty Acid Triglycerides, US Patent Application 20120208967, 2012.
37. 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.
38. Birukov O., Beilin D., Figovsky O., Leykin A., Shapovalov L., Nanostuctured Hybrid Oligomer Composition. US Patent 7,820,779 B2, 2010.
39. Olang F. N., Hybrid Polyurethane Spray Foams Made with Urethane Prepolymers and Rheology Modifiers. US Patent Application 2012/0183694, 2012.
40. 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.
41. 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.
42. Figovsky O., Potashnikov R., Leykin A., Shapovalov L., Sivokon S, Method for Forming a Sprayable Non-Isocyanate Foam Composition, US Patent 20150024138 A1.