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ADVANCES IN THE FIELD OF NONISOCYANATE POLYURETHANES BASED ON CYCLIC CARBONATES

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Abstract. The article reviews production and application of the nonisocyanate polyurethanes based on cyclic carbonate oligomers. Nonisocyanate polyurethane (NIPU) networks are obtained by the reaction between the polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. The result is a crosslinked polymer with β-hydroxyurethane groups of different structure defined as a polyhydroxyurethane polymer. The article discusses NIPU and hybrid NIPU (HNIPU), which also contains epoxy and acrylic compounds. Significant attention was paid to the formation of the materials based on renewable raw materials. The authors provide an overview of the recent publications in this field with a more detailed description of the Polymate Ltd. achievements.

Keywords: nonisocyanate polyurethane, cyclic carbonate, network.

1. Introduction

Polyurethanes (PU) are among the most demanded polymers required by modern technologies [1]. However, the use of toxic components, such as isocyanates, in the fabrication process renders PU production extremely toxic and dangerous [2].

Nonisocyanate sources for PU production have been sought for a long time. Nonisocyanate polyurethanes (NIPU) on the base of polycyclic carbonates and polyamines are known for more than 50 years. Fundamentals for the practical application of NIPU coatings, sealants, adhesives, *etc*. were largely developed by O. Figovsky in the 70-80's [3]. Recently some reviews dedicated to synthesis of cyclic carbonates and NIPU were presented [4-6]. In these works the advantages of NIPU have been described in detail.

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

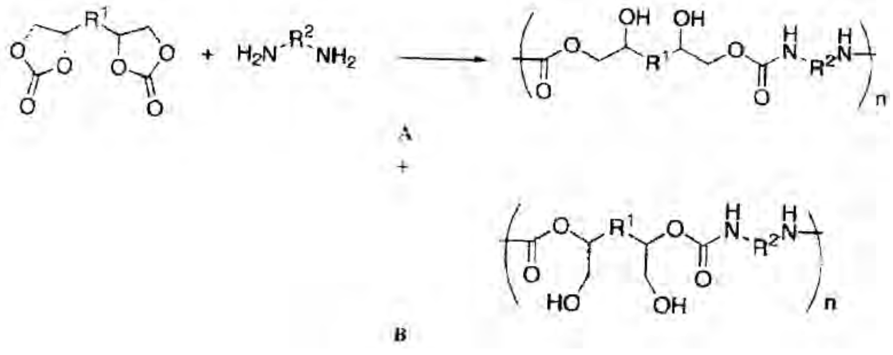


Fig. 1. *b*-Hydroxyurethane moieties of nonisocyanate polyurethanes: with secondary hydroxyl groups (A) and with primary hydroxyl groups (B)

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

Nonetheless, for more than 50 years since the first publication in this field, NIPU still do not have 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, CC reacts only with primary amino groups, in contrast to ER, which reacts with primary and with secondary amino groups. This results into a decrease in crosslinking density of the polymer network.

2. Brief Description of Recent Works in the Field of NIPU

Significant problem of the NIPU technologies is unavailability of the commercially available multifunctional cyclic carbonates. Recent work in the field of new methods for preparing the cyclic carbonates is dedicated primarily to the development of new catalytic systems and the synthesis of monofunctional compounds (see for example reviews [10, 11]). Similar catalyst systems are also used for the copolymerization of epoxides and CO_2 and ring-opening polymerization of cyclic carbonates [12, 13], 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 [14].

Bernard (Rhodia) proposes a method for preparing polyhydroxy-urethanes which comprises the reaction 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 [15]. The subject of this invention is to propose predominantly aqueous formulations on the base of polyfunctionalized polyhydroxy-urethane intermediates, as well as a method for preparing the above-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 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 [16]. But in this case the component (A) also comprises 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 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.) [17] describes a curable composition comprising: a) the mixture of an epoxy resin and cyclic carbonate, and b) a curing agent for 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 [18].

Also researches of Huntsman Co. proposed filled compositions on the base of NIPU or HNIPU and nano-clays [19]. In this work some of synthesized in Polymate Ltd. cyclic carbonates (as raw materials) were used.

Klopsch *et al.* (BASF) disclose the use of new cyclic carbonates with unsaturated bonds as reactive diluents in epoxy resin compositions [20]. It has been found that the 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 [21].

One of the current priorities in polymer chemistry is to explore biobased polymers from renewable resources. Among those polymers, vegetable oils are expected to be an ideal alternative chemical feedstock, owing to their low cost and environmental friendliness [22]. 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 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 the 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 [23]. 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) [24]. 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 a 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 on polyaddition of diamines with vegetable-based biscarbonates to prepare new polyurethanes. The intermediate material (epoxidized compounds were obtained in two steps by transesterification) is conducted starting from monoalkyl esters of unsaturated acids and diols, with subsequent epoxidation. Then the biscarbonates were prepared from difunctional epoxides and supercritical CO_2 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 [25, 26]. Metathesis reaction with Hoveyda’s catalyst was used for preparation of bicarbonates with terminal cyclic carbonate groups.

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 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 [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. Then these intermediates are reacted in a second step with the ethylene carbonate to yield hydroxyl terminated di-urethanes, which then undergo transurethane polycondensation at 423 K 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 of the direction of silicon-contained and nano-structured hydroxyurethane compounds (see our previous review [5]). Turkish researchers synthesized a novel carbonate-modified bis(4-glycidyloxy phenyl) phenyl phosphine oxide (CBGPPO) for preparing the 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 [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 5-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].

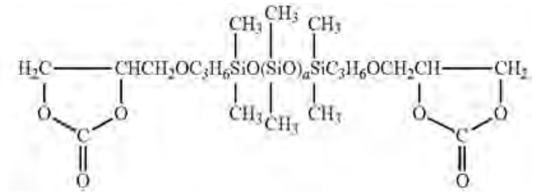


Fig. 2. Example of five-membered cyclic carbonate polysiloxane compound

3. Recent Achievements of Polymate LTD

3.1. Polyhydroxyurethanes

Usually polyhydroxyurethane polymer has poor water resistance 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 cyclocarbonate acrylic polymers were prepared with high water and weather stabilities. A paint was developed with the curing temperature 383 K, in 2–3 h. 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, 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™) 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 polyhidroxy 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

Table 2

Composition and properties of flooring compounds

Composition	F1	F2
	Parts by weight	
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	40.0	45.0
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		
Mixed viscosity, 298 K, mPa·s	970	1450
Pot-life, 298 K, min	30–60	30–60
Tack free, 298 K, h	6	4
After 7 days room temperature, substrate – concrete		
60° Film gloss	115–120	100–105
Hardness, Shore D	70–80	70–80
Tensile strength, MPa	60–70	50–60
Elongation at break, %	3–4	5–7
Taber abrasion, 1000 cycles/1000 g, CS-17 wheel, mg	29	27
Impact resistance, N·m, ≥	20	20

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

3.2. Hybrid Nonisocyanate Polyurethanes

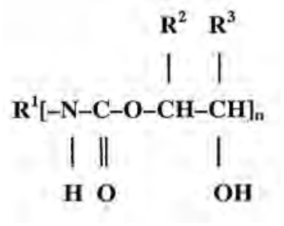
Recently the authors proposed compositions based on oligomer systems which contain a hydroxy-amine adducts on the base of aliphatic mono- and polycyclic carbonates (Cycloate A™) as hardeners [32]. These compositions used for 100 % solid floorings have high abrasion resistance and mechanical properties. Thus Polymate has developed the practically used formulations on the base of HNIPU, for example F1 and F2 (Table 2).

3.3. Hydroxyurethane Modifiers (HUM)

A separate area of the NIPU-technology is the use of pure hydroxyalkyl urethane compounds. Now 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 [5].

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

Our patent application [33] discloses 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 Fig. 3:



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

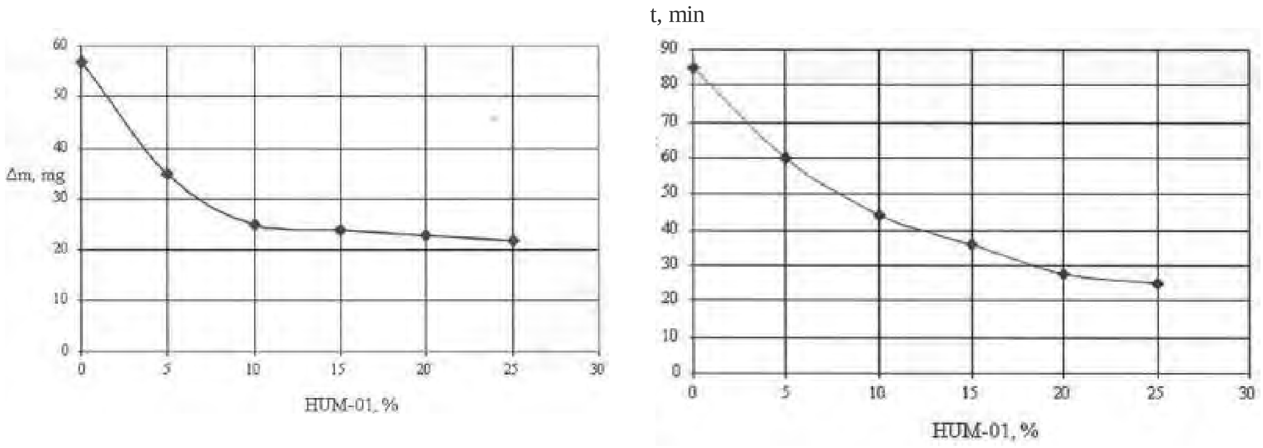
Fig. 3. Basic formula of hydroxyalkyl-urethane modifier (HUM)

where 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: $n \geq 2$.

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 the superior coating performance characteristics (pot-life/drying, strength-stress properties, bonding appearance in a well-balanced state to a variety of substrates). Since the structure of the polymer network is not broken, other characteristics, such as weathering and chemical resistance, do not worsen.

Dependences of curing characteristic and abrasion resistance from content of HUM-01 are shown in Fig. 4 [34].

The following sections provide examples of successful application of HUM into other oligomeric systems.



Abrasion resistance

Pot-life

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

3.4. Hydroxyurethane Compounds from Renewable Plant-Based Raw Materials

Recently the authors proposed a new method of producing 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 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 Fig. 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 time of synthesis and improve quality of the final products.

3.5. 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 the authors have studied new types of NIPUs based on cyclic carbonate-epoxy resin systems and aminoalkoxysilanes [36]. The proposed dendro-amino-silane hardeners give the possibility for the introduction of siloxane fragments into the aromatic structure of BPA epoxy-amine and cyclocarbonate network polymers which improve 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 amount sufficient to bring about substantial hydrolytic polycondensation of the silane [5].

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 [37]. The composition is highly curable at low temperatures (approximately 283 to 303 K) with generating of nanostructure (Fig. 6) under the influence of forming active, specific hydroxyl groups by the reaction of cyclic carbonates with amine functionalities. These hydroxyurethane functionalities activate the 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.

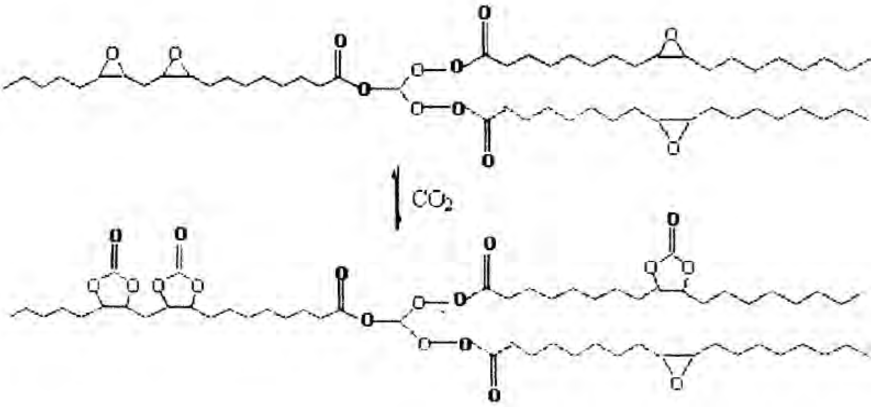


Fig. 5. Obtaining of carbonated-epoxidized unsaturated fatty acid triglycerides

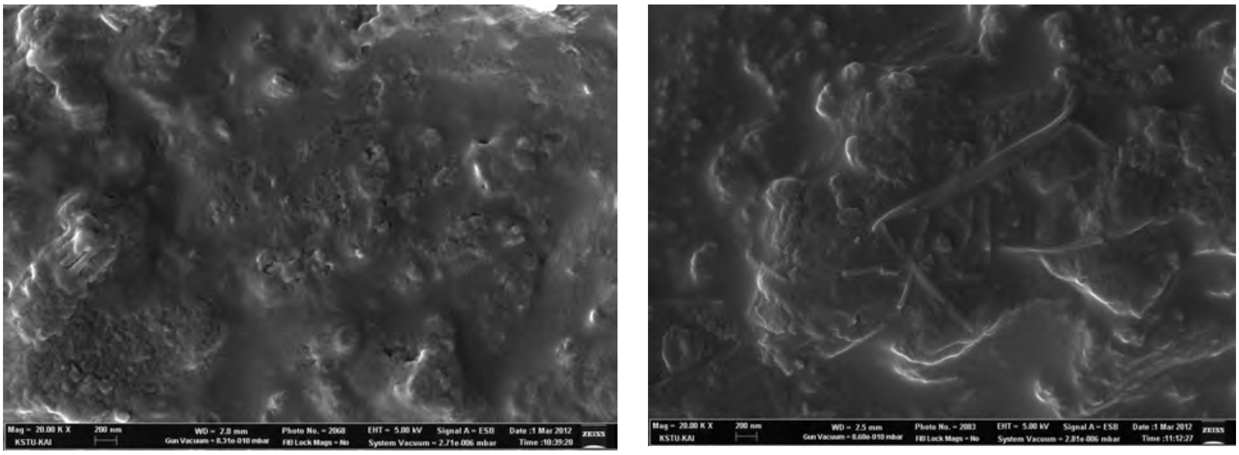

a) b)

Fig. 6. Images of the fractured surfaces of the cured compositions at 20000x magnification (AURIGA CrossBeam): neat epoxy-amine composition (a) and epoxy-silane-amine composition (b)

3.6. 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 the polyurethane foam with open pores). Possibility of application by spraying was tested on the pilot equipment.

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 properties not inferior to polyurethane foams. The foams were produced only in the laboratory (Table 3).

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 is usually 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 cleanability, little odor, and the ability to coat under cold conditions.

The surface preparation and application of UV coatings are similar to those 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 the 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 wear 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 3

Rigid HNIPU foam

Properties	Standard	Rigid foam insulation
Viscosity (Brookfield RVDV II, Spindle 29, 20 rpm) at 298 K, cP	ASTM D2393	
Base "A"		2800–3200
Base "B"		3600-4100
"A" + "B" (3–5 s after mixing)		≤3700
Pot life at: 298 K (77 ºF), 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
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, hr.ft^{2o}F/Btu.in	C 518	4.5–5.0

Table 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, 1000 grams, 1000 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
No. of layers		2+	1

4. Conclusions

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

For further developments in the field of polyhydroxyurethanes, the authors believe that the most promising are the following directions of the research:

1. Creation of polyfunctional cyclocarbonates production, 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 amines production 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.

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ДОСЯГНЕННЯ В ОБЛАСТІ НЕІЗОЦІАНАТНИХ ПОЛІУРЕТАНІВ НА ОСНОВІ ЦИКЛІЧНИХ КАРБОНАТІВ

Анотація. *Розглянуто виробництво і можливість застосування неізоціанатних поліуретанів на основі циклічних карбонатних олігомерів. Неізоціанатні поліуретанові сітки (НІПС) отримували за реакцією між поліциклічними карбонатними олігомерами і аліфатичними або циклоаліфатичними поліамінами з первинними аміногрупами. Отримано зшитий полімер з β-гідроксиуретановими групами різної структури, який представлено як полігідроксиуретановий полімер. Розглянуто НІПС і гібридні НІПС (ГНІПС), що містять також епоксидні і акрилові сполуки. Значну увагу приділено формуванню матеріалів на основі поновлюваної сировини. Приведений огляд останніх публікацій в цій області з докладним описом досягнень* Polymate Ltd.

Ключові слова: *неізоціанатний поліуретан, циклічні карбонати, сітка.*