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## SYNTHESIS AND APPLICATION OF NONISOCYANATE POLYURETHANES

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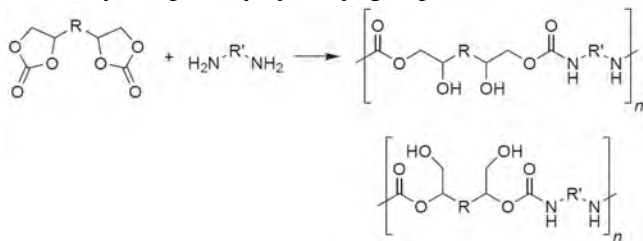
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**Abstract.** The latest published achievements in the research and developments of non-isocyanate polyurethanes on the base of five-membered cyclic carbonates and amines are briefly presented. Preparations of hybrid epoxy-amine hydroxyurethane-grafted polymers with a controlled number of cross-links are described. Examples of the use of hydroxyurethanes of different nature for modification of the oligomeric compositions are also given.

**Keywords:** non-isocyanate polyurethanes, hybrid hydroxyurethane-grafted polymers.

### 1. Introduction

In recent years, intensive research and development are carried out for preparing isocyanate free urethanes and polyurethanes. Some reviews dedicated to synthesis of non-isocyanate urethanes and non-isocyanate polyurethanes (NIPU) on the base of reaction “five-membered cyclic carbonate – amine” have been presented [1–8]. Fig. 1 shows the basic reaction for producing hydroxyurethane (HU) functionalities to form the secondary and primary hydroxyl groups.



**Fig. 1.** Scheme of cyclic carbonate – amine interaction

Different research collectives are making significant efforts to produce NIPU materials suitable for practical use (coatings, foam, adhesives, sealants, *etc.*). The main areas of research and development are polymers

with HU groups in the main chain, graft copolymers with HU groups in the side chains and oligomeric compositions modified by HU-containing additives. From raw material point of view, researchers pay great attention to renewable resources, as well as the use of silicon-organic compounds.

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

European scientific centers are continuing to develop and research NIPU materials.

Research group of the Institute Charles Gerhardt, Montpellier, France (B. Boutevin, S. Caillol and co-workers), and BOSTIK (France) synthesized series of polyHU (PHU) materials by step growth polymerization of polypropylene oxide dicyclic-carbonates (PODC) and diamines in the presence of trimethylolpropane tricyclic carbonate (TMPTCC) used as a crosslinking agent. PHUs exhibit outstanding adhesion properties due to the presence of hydroxyl groups hanging off the main polycarbonate chain [9]. The resulting mechanical and adhesion properties of PHU are consistent with the results previously obtained in Polymate [1, 10].

Several recent works of the Montpellier's team focus on NIPU foam [11–13]. Room temperature flexible PHU foam was developed on the base of the same raw materials for the polymer matrix (PODC, TMPTCC, etherdiamine) [11]. Besides, thiourea as catalyst and poly(methylhydrogen siloxane) as a blowing agent were used for synthesis. In the works [12, 13 (performed in conjunction with Cracow University, Poland)] bio-NIPU foams based on renewable raw materials (cardanol diepoxide and fatty diamine) were presented.

Researchers from Belgium and Canada also used bio-based components for preparation of NIPU foam [14]. The CO<sub>2</sub>-sourced monomers, which were derived from

poly(ethylene glycol) diglycidyl ether (PEG) and epoxydized soybean oil (ESBO), were first prepared by coupling CO<sub>2</sub> with epoxides using a bicomponent organocatalyst composed of an onium salt and a fluorinated alcohol. The NIPUs were then prepared by melt step-growth polymerization with a biosourced amino-telechelic oligoamide. The CO<sub>2</sub>-blown NIPU foam was obtained by the two-step batch foaming method. This consisted of impregnating the NIPU samples with CO<sub>2</sub> under supercritical conditions before their expansion at the temperature of 353 K.

Mülhaupt and co-workers (Freiburg, Germany) [15] presented a versatile process for producing NIPU foam prepared by curing trimethylolpropane-based cyclic carbonate blends with hexamethylene diamine in the presence of fluorohydrocarbon as an environmentally safe physical blowing agent with no ozone depletion potential. Their robust NIPU foam process affords a great variety of tailored soft, flexible, semirigid, and rigid foam.

It should be noted that all the above foams are inferior in properties to the foam elaborated by Polymate [1, 16].

One else direction of the Montpellier's team work is synthesis of amine-terminated PHU and use it for curing polyepoxides [17]. (It should be noted that such technology has developed in the 1960–80's; see, for example, review of patents in [2]). PHU prepolymers were prepared from poly(propylene oxide) bis-carbonate and different excess of ethylenediamine. Excess of ethylenediamine was allowed to terminate the prepolymers by amine and control the degree of polymerization of these oligomers. These properties were demonstrated by a model study and analyzed the structure of oligomers. Then, PHU oligomers were re-used with epoxy compounds to formulate at 323 K polyepoxyurethane polymers. These materials were then studied by characterizing the degree of crosslinking and thermal properties. The thermal characterizations of the materials depend on the chain length of oligomers and the nature of epoxy compounds. These epoxyurethane materials formulated in this study have good thermal properties compared to polyurethane and nonisocyanate polyurethane materials. The main advantage of this technology is the ability to obtain PHU materials with a sequence of soft and hard segments as for classic polyurethanes.

The joint work of several universities (France, Germany) urea- and thiourea-catalyzed aminolysis of carbonates has been studied [18]. This study demonstrates that readily available and affordable urea derivatives may advantageously replace thiourea derivatives or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in the aminolysis of carbonate reactions. This observation renders the NIPU synthesis more appealing as equally performed but cheaper catalysts may be used. Further developments

towards the use of more soluble urea organocatalysts for NIPU syntheses are currently under investigation in their laboratories.

The synthesis of sustainable NIPU on the base of furan-bearing HUs was described in the works [19-20]. Karateev and co-workers (Ukraine) have synthesized furan-bearing PHUs of linear and crosslinked structures based on furfuryloxypropyl cyclocarbonate (FOPCC) and diamine or FOPCC, triamine and furfuryl glycidyl ether respectively. In the second stage both thermally reversible PHUs, due to Diels-Alder (D-A) reaction with bismaleimides, and thermally irreversible PHUs, due to the ion radical polymerization in the presence of complex onium catalyst (Et<sub>3</sub>PhCH<sub>2</sub>N·FeCl<sub>4</sub>) have been obtained [19]. Synthesis conducted by Montpellier's team includes other order of reactions [20]. Firstly dicyclocarbonate D-A adduct of FOPCC and polyether bismaleimide was synthesized. Further a thermo-cleavable NIPU has been synthesized by polymerization of the D-A adduct and polyether diamine. Two main difficulties emerged for this pathway: maleimide reactivity towards amines combined with D-A adduct sensitivity to the temperature. As a consequence, the strategy was to bring cyclocarbonate functionality using furanic compounds and to use a telechelic bismaleimide. The step growth polymerization of cyclocarbonate and amine, despite its low reactivity, was performed at room temperature with a TBD catalyst.

One of the studies in Montpellier was a devoted reaction of cyclic carbonate with amine at 353 K. [21]. The presence of numerous side reactions creating new compounds and non-reactive chain ends such as ureas, oxazolidinones, and alcohols was demonstrated. These latter compounds can be involved in the incapacity to reach high molar masses during the polyaddition reaction of difunctional reactants. The initial stoichiometric ratio is destroyed by the side-reaction of amines with urethane units. These reactions are involved from the very early stages of the reaction and are responsible for the low molar masses of the final polymer.

Effective raw materials for NIPU are multifunctional amino alcohols (AAs) as bio-based curing agents from limonene dioxide and various bio-based glycidylethers, derived from glycerol, trimethylolpropane and pentaerythritol by aminolysis with ammonia. The identical bio-based epoxy raw material is employed to prepare both polyfunctional cyclic carbonates by catalytic conversion with carbon dioxide and the corresponding AA curing agents. Hence, it is possible to produce novel families of 100% bio-based NIPU from the same bio feed stock [22].

Organic/inorganic NIPU hybrid materials are also the focus of researchers. Freiburg's group report on the facile synthesis of novel multifunctional polyhedral oligomeric silsesquioxane (POSS) cyclic carbonates and

their cure with diamines to produce POSS/NIPU nanocomposites with variable POSS content [23].

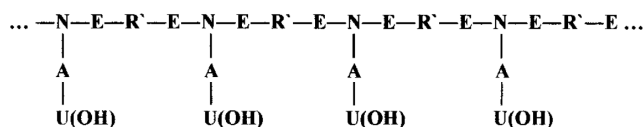
Japanese researchers disclosed a polysiloxane-modified polyhydroxy polyurethane resin derived from a reaction between 5-membered cyclic carbonate polysiloxane compound and an amine compound, and its production process [24]. This resin is excellent in properties such as lubricity, abrasion resistance, chemical resistance, non-tackiness, antistatic properties and heat resistance and is useful as a raw material for film and molding materials, various coating materials and various binders.

A simple and versatile route for the preparation of self-adhesive, corrosion-resistant and photochromic hybrid coatings is presented by Brazilian researchers [25]. The coatings are based on aliphatic poly(dimethyl siloxane)-derived hydroxyurethanes (PDMSUr), produced by the isocyanate-free route for inorganic substrates such as glass and metal alloys. This route involves the ring opening polymerization of a PDMS-derived bis(cyclic carbonate) (CCPDMS) with diamines and aminosilane. The cyclic carbonate was synthesized by cycloaddition of CO<sub>2</sub> into PDMS diglycidyl ether. The use of aminosilanes with CCPDMS enables hybrid organic-inorganic urethanic coatings to be obtained by the sol-gel process.

Thus, it can be concluded that the developers prefer non-hydrolysable alkyl siloxanes for synthesis of hybrid organic-inorganic NIPU materials.

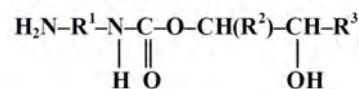
### 3. Hybrid Epoxy-Amine Hydroxyurethane-Grafted Polymer

Preparing of polymers with a specific topological structure of polymer chains is a perspective way of creating materials with needed properties. Recently Polymate Ltd. develops new hybrid HU-grafted polymers with lengthy epoxy-amine chains and pendulous HU units (Fig. 2) [26].



**Fig. 2.** Schematic structural formula of the linear block of the hybrid HU-grafted polymer: **R'** is a residue of the diglycidyl ether, which reacted with amine hydrogens; **E** is a converted epoxy group, i.e.,  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-$ ; **N** is a nitrogen atom; **A** is a residue of a di-primary amine; **U(OH)** is a hydroxyurethane group, i.e.,  $-\text{NH}-\text{CO}-\text{O}-\text{CH}(\text{R}^2)-\text{CH}(\text{OH})-\text{R}^3$ , and  $=\text{N}-\text{A}-\text{U}(\text{OH})$  is a residue of aminohydroxyurethane with the number of free amine hydrogen atoms equal to 2

In turn, aminohydroxyurethane is a product of a reaction of di-primary amine and monocyclic carbonate at the equimolar ratio, i.e., two primary amine groups are accounted for one cyclic carbonate group (Fig. 3).



**Fig. 3.** Aminohydroxyurethane: **R**<sup>1</sup> is a residue of the di-primary amine or polyamine that may consist of additional free amine hydrogen atoms; **R**<sup>2</sup> and **R**<sup>3</sup> are selected from the group consisting of H and alkyl, and at least one of **R**<sup>2</sup> and **R**<sup>3</sup> is hydrogen

In addition to linear units HU-grafted polymers by novel structure may have a controlled number of cross-links and combine increased flexibility with well-balanced physico-mechanical and physico-chemical properties of conventional epoxy-amine systems [27].

The process of obtaining and properties of the polymers are described below.

#### 3.1. Objects and Methods

The following commercially available raw materials were used:

- epoxy resins and glycidyl ethers: D.E.R.® 331 (standard diglycidyl ether of bisphenol A, EEW = 187), D.E.N.® 431 (epoxy-novolac resin, EEW = 175), D.E.R.® 737 (diglycidyl ether of cyclohexanedimethanol, EEW = 175), D.E.R.® 738 (diglycidyl ether of neopentyl glycol, EEW = 155) all produced by Olin Corp.; epoxy resin ST-3000 (hydrogenated DGEBA, EEW = 230) produced by KUKDO Chemical Co.; Heloxy® 48 (triglycidyl ether of trimethylol propane, EEW=145) produced by Hexion Specialty Chemicals Inc.;

- cyclic carbonate: Jeffsol® PC (propylene carbonate, CCEW = 102) produced by Huntsman Corp.

- di-primary and polyfunctional amines: Vestamin® TMD [2,2,4(2,4,4)-trimethylhexamethylene diamine] produced by Evonik; Jeffamine® D400 (polyoxypropylene diamine, AEW = 230, AHEW = 115) and Jeffamine® T403 (polyoxypropylenetriamine, AEW = 162, AHEW = 81) both produced by Huntsman Corp.; PolyTHF® Amin 350 (polytetrahydrofuranamine, AEW = 160.3, AHEW = 88) produced by BASF; MXDA (meta-xylylenediamine, AEW = 68, AHEW = 34) produced by Mitsubishi Gas Chemical Comp.; D.E.H.® 20 (diethylenetriamine, AEW = 51.5, AHEW = 20.6) produced by Olin Corp.

Abbreviations used:

- 1) EEW – epoxy equivalent weight;
- 2) AEW – primary amine equivalent weight;

- 3) AHEW – amine hydrogen equivalent weight;
- 4) CCEW – cyclic carbonate equivalent weight;
- 5)  $f$  – functionality of the components.

Reactions between cyclic carbonate and primary amine groups were monitored by Nicolet 380 FT-IR spectrometer according to cyclic carbonate  $\nu_{C=O}$  band at  $1800\text{ cm}^{-1}$ .

Dynamic viscosity was determined on the Brookfield VN-II+ viscometer. Pot life of compositions was determined according to ASTM D1084 as the time during which the viscosity is doubled.

The polymerized samples were tested with regard to the following mechanical and chemical properties: tensile strength and ultimate elongation were performed on the unit Lloyd LR 50K according to ASTM D638M at a speed of 50 mm/min; hardness (Shore D) was determined on durometer CV (SHD0002, Bowers) according to ASTM D2240; weight gain at immersion in water (24 h at 298 K) was determined in accordance with ASTM D570; weight gain at immersion in 20%  $\text{H}_2\text{SO}_4$  (24 h at 298 K) was determined in accordance with ASTM D543.

### 3.2. Synthesis of Aminohydroxyurethane

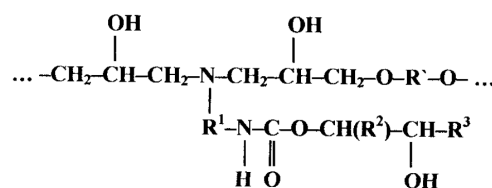
Aminohydroxyurethanes (intermediate products, Fig. 3) with the number of free amine hydrogen atoms equal to 2 were synthesized from PC and different amines in a 500 ml glass reactor equipped with a stirrer and a heater (Table 1).

### 3.3. Synthesis of the Hybrid Epoxy-Amine Hydroxyurethane-Grafted Polymers

The hybrid epoxy-amine hydroxyurethane-grafted polymer of a novel structure is obtained by curing a liquid oligomer composition which consists of diglycidyl ether and aminohydroxyurethane (Fig. 2) with the number of free amine hydrogen atoms equal to 2, wherein the diglycidyl ether and aminohydroxyurethane are at stoichiometric ratio of glycidyl groups and free amine hydrogen atoms.

Curing of the grafted polymers (Table 2) was performed at RT for 7 days.

A presumed structure of the main backbone of the novel epoxy-amine HU-grafted polymers can be presented by the following formula (Fig. 4).



**Fig. 4.** Main backbone of the epoxy-amine HU-grafted polymer (designations being the same as above)

The schematic structural formula of the polymers according to examples 1-4 is presented in Fig. 2.

Table 1

**Description of the intermediate hydroxyurethane-amines**

Name of product	Amine	AEW/CCEW ratio	AHEW of product	$f$	Viscosity (298 K), Pa·s
HUMA-1	TMD	2 : 1	130	2	9.15
HUMA-2	MXDA	2 : 1	119	2	1.48
HUMA-3	D-400	2 : 1	281	2	0.45
HUMA-4	PTHFA	2 : 1	226	2	0.7
HUPA-1	T-403	3 : 1	147	4	3.74
HUPA-2	DETA	2 : 1	68.3	3	6.7

Table 2

**Description of the grafted polymers**

Example No.	Intermediate hydroxyurethane-amine	Epoxy resin	Cross-linking agents	
			amine	epoxy
1	HUMA-1	DER 737	–	–
2	HUMA-2	DER 738	–	–
3	HUMA-3	DER 331	–	–
4	HUMA-4	ST-3000	–	–
5	HUMA-1	DER 331	HUPA-1	H48
6	HUMA-2	DER 737	HUPA-2	DEN 431

Table 3

Properties of compositions (examples 1-6)

Measured characteristics	Example No.					
	1	2	3	4	5	6
Pot life, min	60	40	60	50	25	30
Hardness, Shore D	15	20	35	20	44	60
Tensile strength, MPa	1.1	0.9	3.0	2.4	12	10
Elongation at break, %	147	130	275	183	72	73
Weight gain at immersion in water (24 h at 298 K), %	1.1	1.8	0.3	0.3	0.2	0.1
Weight gain at immersion in 10% NaOH(24 h at 298 K), %	1.1	1.4	0.6	0.5	0.3	0.1

Table 4

Main Properties of Synthetic Leather

Sample	Fabric type	Tensile strength, MPa	Elongation, %	Cold crack resistance, K
A	non-woven synthetic soft	70	45	253
B	non-woven synthetic hard thin	76	33	253
C	thin synthetic knitwear	24	155	253

Table 5

Composition and properties of HUMs for RC compounds

HUM	Raw materials		Viscosity at 298 K, mPa·s
	Cyclic carbonate	Primary amine	
Priamine-PC	Jeffsol® PC (Huntsman)	Priamine™ 1071 (Croda)	1200
AMEO-PC		Dynasylan® AMEO (Evonik)	115
1505-PC		Dynasylan® 1505 (Evonik)	95
AMMO-PC		Dynasylan® AMMO (Evonik)	130

Alternatively, the hybrid epoxy-amine HU-grafted polymer may also have a number of cross-links obtained by introducing into the initial composition some polyfunctional components for controlling the number of cross-links (examples 5-6) [27]. The polyfunctional components may comprise polyglycidyl compounds with the functionality more than 2, aminohydroxyurethanes of formula 2, wherein R<sup>1</sup> is a residue of the polyamine, with a number of free amine hydrogen atoms more than 2, and combinations thereof in amounts of 20–25 eqv. %.

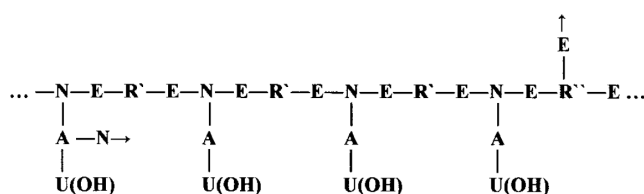


Fig. 5. Schematic structural formula of the cross-linked

block of the hybrid HU-grafted polymer: E-R''-E is a residue of the polyfunctional epoxy resin, other designations being the same as above. Polyamines with a number of free amine hydrogen atoms more than 2 were also used for cross-linking

A schematic structural formula of the novel polymer according to examples 5-6 with the directions of the possible cross-links (shown by arrows) is shown in Fig. 5.

The results of the tests of the hybrid epoxy-amine hydroxyurethane-grafted polymers are summarized in Table 3.

### 3.4. Testing of Synthetic Leather

The coating formulations for imitation leathers, which contained the components described in Examples 1–3, were separately applied onto paper sheets and cured by drying to form on the paper substrate films of incompletely cured polymer coating having a thickness of 25 μm. The coated products were cut into separated pieces, applied onto fabric substrates (see Table 3) and bonded to the substrates under pressure developed by a load. After bonding to the fabric and solidification of the coating, the paper substrates were peeled off. As a result, samples A, B, and C of the synthetic leather shown in Table 4 were obtained.

Tensile properties of the samples were determined according to ASTM D638. Cold crack resistance was

measured according to CFFA-6 (Standard Test Methods. Chemical Coated Fabrics and Film. Chemical Fabrics & Film Association, Inc. Cleveland, 2011).

The hybrid epoxy-amine HU-grafted polymer No. 1 was used as in Sample A, the hybrid epoxy-amine HU-grafted polymer No. 2 was used as in Sample B, the hybrid epoxy-amine HU-grafted polymer No. 3 was used as in Sample C.

#### 4. Hydroxyurethane Modifier (HUM)

It is known that HU compounds are used as modifying agents, which do not react chemically with other components.

Patent [28] discloses three-dimensional epoxy-amine polymer networks modified by a hydroxyalkyl urethane, which is obtained as a result of a reaction between a primary amine (one equivalent of the primary amine groups) and a monocyclic carbonate (one equivalent of the cyclic carbonate groups). Such hydroxyalkyl urethane modifier is not bound chemically to the main polymer network and is represented by the following formula:

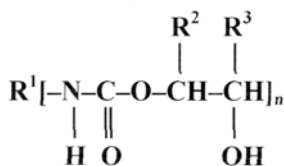


Fig. 6. HUM (designations being the same as above)



Fig. 7. HUM of vegetable origin:  $\text{R}^1$  is a residue of the biobased primary amine, selected from the group consisting of  $\text{C}_{36}$ -dimer fatty acid, diamine hydrogenated, and mixture of  $\text{C}_{36}$ -dimer fatty acid, diamine hydrogenated with trimer fatty acid, triamine hydrogenated;  $\text{R}^2$  and  $\text{R}^3$  are the same as stated above



Fig. 8. HUM, based on aminosilanes:  $\text{R}^2$  and  $\text{R}^3$  are the same as stated above,  $\text{R}^4$  is generally an aliphatic group having from 1 to 6 carbon atoms,  $\text{R}^5$  and  $\text{R}^6$ , independently, are hydrocarbon radicals containing from 1 to 20 carbon atoms and selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups or combinations thereof, and  $n$  is equal to 1, 2, or 3

HUMs of different nature were used in radiation-curable (RC) compositions [29].

The bases of the composition are (meth)acrylic monomers and oligomers, including (meth)acrylated oils,

and photoinitiators. The authors propose the use of nonreactive modifiers, which are not cured by radiation and do not react chemically with other components of compositions. At the same time, these additives contain functional groups, positively affecting the set of properties of the RC compositions.

Used as an additive is a PHU (nonisocyanate) composition comprising the combination of HU, preferably diHU, based on diamines of vegetable origin (Fig. 7) and hydroxyurethane, preferably monohydroxyurethane, based on aminosilanes (Fig. 8).

Examples of the nonreactive HUM are presented in Table 5. The aforementioned additive improves a combination of properties of RC compositions, such as appearance, abrasive resistance, and adhesion to a substrate. Furthermore, without deterioration of other properties, the additive may increase the thickness of a coating that is cured in one pass. The inventive methodology is directed to advanced RC compositions, especially for flooring on the surfaces of concrete, asphalt, etc. The invention also involves an extensive use of raw materials that are based on renewable resources.

#### 4. Conclusions

It is evident from the present review that considerable effort has been made during the last years to develop environmentally friendly methods of obtaining polymer materials containing urethane groups. Fabrication of NIPUs on the base of multicyclic carbonates and polyamines is difficult because of necessity to use toxic solvent and high temperatures and also insufficient water resistance.

The use of renewable raw materials is faced with a serious problem of its standard.

The most promising method is obtaining HNIPUs based on modification of different polymers by NIPU fragments. Hybrid coatings, comprising epoxy matrix modified by NIPU, are commercially available under the name of Green Polyurethane™ as an isocyanate-free and phosgene-free alternative to conventional materials and represent the first successful application of HNIPUs in industry. As it was stated by "Hybrid Coating Technologies" [30], HNIPUs offer several advantages with respect to conventional polyurethanes. They are solvent-free, more resistant to chemical degradation, 20 % more wear resistant, can be applied on wet substrates, and cured under cold conditions. They exhibit up to 30 % higher adhesion than that of conventional polyurethane.

A method of synthesis of novel polymers with lengthy epoxy-amine chains, pendulous hydroxyurethane units and a controlled number of cross-links was proposed. Cured hybrid epoxy-amine hydroxyurethane-

grafted polymer with presumably linear structure was prepared.

Testing of hybrid polymers demonstrate the increased flexibility with well balanced physico-mechanical and physico-chemical properties of conventional epoxy-amine systems. In particular, new materials have tensile strength up to 12 MPa and elongation at break 70–275 %. They may be used for various applications, for example, for manufacturing of synthetic / artificial leather, soft monolithic floorings and flexible foam.

These authors' elaboration of non-isocyanate polyurethanes was awarded by the NASA Nanotech Briefs®, Nano 50™ Award (USA) and 2015 Presidential Green Chemistry Challenge Award (USA) [31].

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## СИНТЕЗ І ЗАСТОСУВАННЯ НЕІЗОЦІАНАТНИХ ПОЛІУРЕТАНІВ

**Анотація.** Представлені останні опубліковані досягнення в області досліджень і розробок неізоціанатних поліуретанів на основі п'ятичленних циклічних карбонатів і амінів. Описано приготування гібридних епокси-амінних гідроксиуретан-прищеплених полімерів з контрольованою кількістю зшивок. Наведено приклади використання гідроксиуретанів різної природи для модифікації олігомерних композицій.

**Ключові слова:** неізоціанатні поліуретани, гібридні гідроксиуретан-прищеплені полімери.