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НЕИЗОЦИАНАТНЫЕ ПОЛИУРЕТАНЫ – ВЧЕРА, СЕГОДНЯ И ЗАВТРА*

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Задача данной статьи – систематизировать опубликованные результаты в области неизоцианатных полиуретанов (НИПУ). Основное внимание было уделено замене ими традиционных полиуретанов, отверждаемых при обычных температурах и практически не содержащих летучих органических веществ (ЛОВ). Такие материалы используют в основном при производстве красок, половых покрытий и пен. Рассмотрены возобновляемые источники сырья и другие новые пути синтеза НИПУ. Приведены также сведения о гибридных композициях (ГНИПУ).

Ключевые слова: неизоцианатные полиуретаны, гибридные неизоцианатные полиуретаны, циклокарбонаты, полиамины, покрытия для промышленности и строительства.

NON-ISOCYANATE POLYURETHANES – YESTERDAY, TODAY AND TOMORROW

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In this article we try to systematize the published results in the field of non-isocyanate polyurethanes (NIPUs). The main attention is paid to substitution of conventional polyurethanes cured at ambient temperatures and practically without VOC. Such materials are used mainly in the mass-production of paints, floorings and foam. Sustainable routes and other new ways of NIPU synthesize are described. Also data of hybrid compositions (HNIPUs) are provided.

Keywords: non-isocyanate polyurethanes, hybrid non-isocyanate polyurethanes, cyclic carbonates, polyamines, industrial and architectural coatings.

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

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Публикации: более 200 публикаций, включая 60 изобретений.

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Publications: more than 200 including 60 patents.

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Introduction

Polyurethanes (PUs) are products of the addition polymerization reaction between di- (or poly-) isocyanates and di- (or poly-)ols. PUs are among the most used polymers in many modern applications – foams, coatings, sealants, elastomers, thermoplastics, adhesives, fibers and so on [1].

The polyurethane (PU) market today amounts to about 5 % of the total polymer market and the worldwide consumption of PU has increased steadily. The demand in PUs has continued to increase and it will attain in 2016 a production of 18 million tons (~US$66.4 bln).

However, the use of isocyanates in the manufacturing process can render PU production extremely toxic and dangerous [2]. In fact, these compounds are harmful for human and environment. People exposed to isocyanates can develop a range of short-term health problems. More seriously, isocyanate exposure can lead to long-term asthma and dermatitis if individuals become sensitized. Sensitization is a condition in which the breathing or skin conditions can return with increasing severity on further exposures to the original sensitizing agent or to similar substances, even at very low exposures [2]. MDI (methylene diphenyl isocyanate) and TDI (toluene diisocyanate), the most widely used isocyanates in PU industry, are classified as CMR (Carcinogen, Mutagen and Reprotoxic) [3].

At the same time, conventional PU have an inherent weakness depending on their molecular composition. Van der Waals forces mainly sets physically and mechanically properties of PU. The strength of these bonds is significantly lower in energy, however [1]. Therefore PU unsatisfactorily stands up to the dynamic load, especially at elevated temperature.

Non-isocyanate sources for PU production have been sought for a long time.

There are several reactions, essentially based on transcarbamoylation, attracted researchers interest due to the possibility to form polyurethanes without isocyanate monomers in the formulations, which complies with the new environment and safety requirements. However these reactions occur at high temperatures and accompanied by the formation of considerable amounts of by-products [4–7].

Non-isocyanate polyurethane (NIPU) based on the reaction of polycyclic carbonates and polyamines are known for more than 50 years. Recently, some reviews dedicated to synthesis of cyclic carbonates (CC) and NIPU have been presented [8–15].

Development of the scientific direction "NIPU based on the reaction of polycyclic carbonates and polyamines" demonstrates a chronological list of patents and applications issued in the field (Table 1). The list also describes the interest of leading companies to commercialize the developments. [Hereinafter patents from the Table 1 are numbered as P1, P2, etc.].

The first patents were obtained in the 1950's (P1-P3).

In the former Soviet Union basic and applied research on the synthesis of CC and NIPU were launched in Institute of Synthetic Rubber (P6-P9). Significant achievements of the researches were development of polymeric acetals by reacting non-isocyanate urethane diols with divinyl ethers (named "Acetur") and creating of NIPU based on elastomeric liquid polydienes.

Mechanical and physical-chemical characteristics of NIPU are inferior to conventional PU, so almost immediately after the first reports of NIPU started developing of hybrid compositions (HNIPU), namely: subsequent cross-linking the resin by reacting with a poly-functional reactant (P4); combining NIPU with epoxy resins and amine hardeners (P5, P6)

Practical application of HNIPU on the basis of the epoxy-amine compositions and five-membered CC (1,3-dioxolan-2-ones) in coatings, sealants, adhesives, etc. were largely developed by O. Figovsky, V. Mikheev, V. Stroganov et al. in the 1970–1990's (P10-P15, P17-P21, P23-P25, P29-P31).

Table

Using the reaction of cyclic carbonate with an amine in the synthesis of non-isocyanate urethane polymers

№	Patent No. / Priority (year)	Applicant(s)/ Inventor(s)	Brief description
1	US 2802022 / 1954	Groszos, et al. / (American Cyanamid)	A method of preparing a polyurethane which comprises reacting together urea and mono- or poly-β-hydroxyurethane on the base of mono- or polyamine and alkylene carbonate.
2	US 2935494 / 1957	Whelan, Jr. et al. / (Union Carbide – today Dow Chemical)	A linear polyurethane product prepared by the reaction of erythritol dicarbonate and a polyfunctional amine.
3	US 3072613 / 1957	Whelan, Jr. et al. / (Union Carbide – today Dow Chemical)	A resinous polyurethane product prepared by the reaction of bis-CC and a polyfunctional amine.
4	US 3084140 /1957	Gurgiolo, et al. / (Dow Chemical)	A polyhydroxy polyurethane resin produced by reacting an aliphatic polyamine and a dicyclic carbonate and subsequent cross-linking the resin by reacting with a poly-functional reactant selected from the group consisting of aldehydes, dicarboxylic acid chlorides, thionyl chloride and sulfuryl chloride and insolubilization of the resin.

5	US 3305527 / 1964	Price (Celanese Coatings)	Combining epoxide resins with 1,2-alkylene carbonates and primary amine curing agents such as ethylene diamine is disclosed.
6	SU 413824 / 1969	Petrov, et al.	Process for preparing polymer materials with a urethane group in the chain by reaction of an epoxy resin with a polyamine containing urethane groups which are obtained by the reaction of a primary or secondary diamine with bicyclic carbonates.
7	SU 359255 / 1971	Petrov, et al.	Non-isocyanate polyurethanes on the base of branched polycyclic carbonates and diamines with M_W = 500-3000 (hydroxyurethane diamines, polyether diamines, polyester diamines, siloxane diamines, branched aminoamides).
8	US 3929731 / 1973	Volkova, et al.	Production of polymeric acetals by reacting non-isocyanate urethane diols with divinyl ethers.
9	GB 1495555 / 1974	Petrov, et al.	Method of producing a polyurethane comprising reacting a hydrocarbon polymer having at least one double bond and from 0.26 to 12.2 mol percent cyclocarbonate groups, with a primary or secondary amine.
10	SU 529197 / 1975	Fedorova, Figovsky, et al.	A polymer floor base comprising epoxy resin, dicyclic carbonate of polypropylene glycol, xylene diamine and mineral filler.
11	SU 563396 / 1976	Figovsky, et al.	Polymer-concrete mix comprising trihydroxyurethane on the base of polyoxypropylene triamine and propylene carbonate, divinyl ether of ethylene glycol, catalyst and mineral fillers.
12	SU 630275 / 1976	Figovsky, et al.	Polymer composition comprising polyoxyalkylenetriol tricyclic carbonate and adduct amine with epoxy resin.
13	SU 668337 / 1977	Movsisyan, Figovsky, et al.	Adhesion sublayer for polyethyleneterephtalate films comprising polyurethane acetals obtained by reacting nonisocyanate urethane-containing glycols with divinyl ethers of glycols.
14	SU 671318 / 1977	Stroganov, Figovsky	Preparing of epoxy-cyclic carbonate resins.
15	SU 704032 / 1976	Figovsky, et al.	Composition of epoxy resin, polyoxypropylenetriol tricyclic carbonate, amine and fillers.
16	US 4122068 / 1977	Meyer (Huntsman)	Resistance to thermal shock of anhydride cured epoxy resins is enhanced by addition of polyether dihydroxyalkyl carbamate additives on the base of polyoxyalkylene diamines (M_W 2000-3000) and monocyclic carbonates.
17	SU 707258 / 1978	Stroganov, Figovsky, et al.	Preparing of epoxy-cyclic carbonate resins.
18	SU 798126 / 1978	Mikheev, et al.	Use of PU-glycols for synthesis of polyesters.
19	SU 903340 / 1978	Kutsenok, Figovsky, et al.	Polymer concrete on the base of hybrid composition: epoxy resin-dicyclic carbonate-amine.
20	SU 908769 / 1978	Figovsky, et al.	Polymer concrete on the base of hybrid composition: epoxy-cyclic carbonate resin and amine.
21	RU 970856 / 1980	Sysoev, Mikheev, et al.	NIPU on the base of aromatic polycyclic carbonates.
22	CA 1247288 / 1982	Hesse (Hoechst)	Epoxy resin based compositions comprise β-hydroxyurethane- modified amine hardeners.
23	SU 1110783 / 1983	Stroganov, Figovsky, et al.	Cyclohexyl cyclic carbonate and corresponding NIPU.
24	SU 1126569 / 1983	Stroganov, Figovsky, et al.	Aryl cyclic carbonates as adhesion additives in epoxy base compositions.
25	SU 1240766 / 1983	Mikheev, et al.	Water-soluble oligomeric urethane from amino-epoxy adduct and monocyclic carbonate and self-curable at 200° C. coatings on the base of thereof.

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26	US 4484994 / 1984	Jacobs III, et al. (American Cyanamid)	Hydroxyalkyl urethane-containing resin having at least one tertiary amine and at least two hydroxyalkyl urethane groups per molecule. The polymer is obtained by reacting an epoxy resin with one or more amines having at least one secondary amine group and at least one hydroxyalkyl urethane group or a precursor thereof.
27	US 4528363 / 1984	Tominaga (Kansai Paint)	Amino-(β-hydroxyurethanes) and epoxy or acrylic compounds as source blocks for heat-curable resin preparation.
28	US 4758632 / 1985	Parekh et al. (American Cyanamid)	A self-cross-linkable acrylic polymer contains at least two hydroxyalkyl carbamate groups per molecule.
29	SU 1587899 / 1988	Figovsky, et al.	Flooring on the base of hybrid composition: aromatic epoxy resin, aliphatic epoxy resin, polyoxypropylenetriol tricyclic carbonate and Mannich base amine.
30	SU 1754747 / 1990	Stroganov, Figovsky, et al.	Flooring on the base of hybrid composition: aromatic epoxy resin, aliphatic epoxy resin, dicyclic carbonate, aminophenol and polyoxypropylenediamine.
31	SU 1754748 / 1990	Figovsky, et al.	Flooring on the base of hybrid composition: aromatic epoxy resin, polyoxypropylenetriol triglycidyl ether, polyoxypropylenetriol tricyclic carbonate and aminophenol.
32	US 5235007 / 1991	Alexander et al. (Huntsman)	A curing agent mixture for epoxy resin compositions comprises a di-primary amine (M_W 60-400) and an amine-carbamate which is the reaction product of an excess of the di-primary amine and a monocyclic carbonate.
33	US 5175231 /1992	Rappoport et al.	A method for preparing a urethane by reacting a compound containing a plurality of cyclocarbonate groups with a diamine in which the two amine groups have different reactivities with cyclocarbonate so as to form a urethane oligomer with amine end groups. The urethane oligomer can then be reacted in different ways to form a polyurethane.
34	US 5340889 / 1993	Crawford et al. (Huntsman)	Liquid hydroxyurethane products having cyclocarbonate end groups are prepared by reacting a molar excess of a bis-carbonate of a bis-glycidyl ether of neopentyl glycol or 1,4-cyclohexanedimethanol with a polyoxyalkylenediamine. These products are useful for the preparation of PU, PU polyols, polyester PU polyols, and polycarbonate PU polyols.
35	US 5677006, US 5707741, US 5855961, US 5935710 / 1993	Hoenel, et al. (Hoechst)	Waterborne coating compositions, including one or more resins having amino-reactive groups, one or more polyamine curing agents, and one or more aminourethanes. The aminourethanes can be reaction products of oligomeric or polymeric compounds containing terminal cyclic carbonate groups, and amines.
36	US 6120905 / 1998	Figovsky, et al.	A hybrid non-isocyanate polyurethane network polymer formed by cross-linking at least one cyclocarbonate oligomer and at least one amine oligomer. The cyclocarbonate oligomer contains a plurality of terminal cyclocarbonate groups. At least one cyclocarbonate oligomer further comprises from about 4% to about 12% by weight of terminal epoxy groups.
37	US 6407198 / 1999	Figovsky, et al. (Polymate)	Chemically resistant materials with high mechanical properties are provided by using polycyclocarbonates of special structure. The polycyclocarbonates are prepared by the reaction of oligocyclocarbonates containing ended epoxy groups with primary aromatic diamine.
38	EP 1070733 / 1999	Figovsky, et al. (Polymate)	Method of synthesis of polyaminofunctional hydroxyurethane oligomers and hybrid polymers formed therefrom.
39	US 7045577 / 2002	Wilkes, et al.	A preparation of novel carbonated vegetable oils (such as carbonated soybean oil) by reacting carbon dioxide with an epoxidized vegetable oil is described. The carbonated vegetable oils advantageously may be used for producing non-isocyanate polyurethane materials.

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40	US 7232877 / 2002	Figovsky, et al.	A star epoxy compounds and their preparation and use in making star cyclocarbonates, star hydroxy urethane oligomers, and star NIPU and HNIPU are disclosed. Acrylic epoxy compounds, acrylic cyclocarbonates, acrylic hydroxy urethane oligomers, acrylic NIPU and HNIPU and their methods of preparation also are described.
41	US 7288595 / 2002	Swarup, et al. (PPG Industries)	A reaction product having polyether carbamate groups formed from polyoxyalkylene amine, and cyclic carbonate, in equivalent ratios ranging from (1:0.5) to (1:1.5) is provided. Further provided is a process for preparing the aforementioned reaction product.
42	US 8143346 and 8450413 / 2003	Diakoumakos, et al. (Huntsman)	A fast curable NIPU and HNIPU polymeric nanocompositions are derived upon crosslinking a mixture comprising of natural or modified nano-clay with either a monomer(s) / oligomer(s) bearing cyclocarbonate group(s) or a mixture of the latter with an epoxy resin, with a hardener bearing amino groups.
43	US 6960619 / 2003	Figovsky, et al.	UV-curable liquid acrylic-based compositions (for sealing applications), which include products of reaction of non-isocyanate urethane diols with metacrylic or acrylic anhydride.
44	US 7842773 / 2006	Herzig (Wacker)	Organosilicon compounds containing non-isocyanate urethane groups are prepared by reacting aminofunctional organosilicon compounds with CC, and, in a second stage, the first stage reaction products are optionally condensed with silanes bearing groups capable of condensation, to give higher molecular weight organosilicon compounds containing urethane groups.
45	US 8017719 / 2007	Bernard, et al. (Rhodia)	Method for preparing polyhydroxy-urethanes from amino compounds and compounds carrying cyclic carbonate functions.
46	US Application 12/315580, 2008	Birukov, et al. (Polymate, NTI)	A liquid cross-linkable oligomer composition that contains a hydroxyurethane-amine adduct and a liquid-reacting oligomer is proposed. The hydroxyurethane-amine adduct is a product of an epoxy-amine adduct reacting with a compound having one or more terminal cyclocarbonate groups.
47	US 7820779 / 2009	Birukov, et al. (Polymate, NTI)	A nanostructured hybrid liquid oligomer composition including at least one epoxy-functional component, at least one cyclic carbonate component, at least one amine-functional component, and, optionally, at least one acrylate (methacrylate) functional component, wherein at least one epoxy, amine, or acrylate (methacrylate) component contains alkoxysilane units.
48	US 7989553 / 2009	Birukov, et al. (Polymate, NTI)	There are disclosed 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.
49	US 9115111 / 2009	Cramail, et al. (C.N.R.S., France)	Synthesis of terminal bicarbonate precursors from plant base raw materials.
50	US 8853322 / 2009	Mecfel-Marczevsky, et al. (BASF)	Water-dispersible, cyclocarbonate-functionalized vinyl copolymer binder and an amine curing agent. In this binder the emulsifier groups are incorporated in the polymer chain, gives stable aqueous dispersions having a solids content of up to a 30% by weight.
51	US 8703648, US 8975420, US 8951933 / 2009	Hanada, et al.	A new polysiloxane-modified polyhydroxy polyurethane resin derived from a reaction between a 5-membered cyclic carbonate compound and an amine modified polysiloxane compound is disclosed.
52	US 8741988 / 2010	Klopsch , et al. (BASF)	Unsaturated monocyclic carbonates as reactive diluents for epoxy resin compositions.

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53	US 8742137 / 2010	Mecfel-Marczevsky, et al. (BASF)	2-oxo-1,3-dioxolane-4-carboxylic acid esters transesterified with a polyol having a valency of 2 to 5 in the presence of an enzymatic catalyst or an acidic cation exchanger and further cured with polyamines.
54	US Application 14/0030526 / 2011	Uruno, et al.	Polyhydroxyurethane microparticles are spherical polymer microparticles having particle sizes of 0.1 μm to 300 μm and have been derived from cyclic carbonates and amines.
55	US Application 20140191156 / 2011	Marks, et al. (Dow Global Technologies)	A novel cyclic carbonate monomer comprising a reaction product of at least one divinylarene dioxide and carbon dioxide. The poly(hydroxyurethane) compositions made from Divinylbenzene Dicarbonate and polyamines forms a reactive intermediate that can be used for making, for example, a poly(hydroxyurethane) foam product having an approximate volume expansion of 10.
56	US 8653174 / 2011	Anderson, et al. (Dow Global Technologies)	Alternative synthesis of NIPU at ambient temperatures from the reaction of polyaldehydes with carbamate functional polymers using an acid catalyst.
57	US Application 20140378648 / 2011	Soules, et al. (University of Montpellier, France)	A method for preparing a compound comprising a β-hydroxy urethane unit or a γ-hydroxy-urethane unit, comprising reacting a compound A comprising a cyclocarbonate reactive unit with a compound B comprising an amino reactive unit (-NH_2) in the presence of a catalyst, said method being characterized in that said catalyst comprises an organometallic complex and a cocatalyst selected from the group of Lewis bases, or salts of tetra-alkyl ammonium.
58	US 8586653, US 8877837 / 2011	Yu, et al. (BASF)	HNIPU on the base of epoxy resins and cyclic carbonates with unsaturated bonds using mixtures of amino hardeners and catalysts.
59	US 9079871 / 2011	Mezger, et al. (BASF)	Preparation of tricycle carbonates by reaction of trioxyalkyl amine with (2-oxo-1,3-dioxolan-4-yl)methyl chloroformate in an aqueous/organic two-phase system in the presence of an auxiliary base and of a phase transfer catalyst.
60	US 9150709 / 2011	Klopsch , et al. (BASF)	HNIPU on the base of epoxy resins, cyclic carbonates with an electron-withdrawing organic group and amino hardeners.
61	US 9062136 / 2011	Porta Garcia, et al. (BASF)	Homo- and copolymers obtained by homo- or copolymerization of alkylidene-1,3-dioxolan-2-one monomers and to the use thereof as a component in 2K binder compositions by crosslinking with amine hardeners.
62	WO 2012171659 / 2011	Bähr, et al. (University of Freiburg, Germany)	Terpene or terpenoid derivatives comprising at least two cyclic carbonate groups and isocyanate-free polyurethanes obtainable form the reaction of monomers with at least two cyclic carbonate groups with amine monomers comprising at least two amino groups.
63	US 9102829 / 2012	Birukov, et al. (Polymate, NTI)	A method of obtaining hybrid polyhydroxyurethane compositions based on unsaturated fatty acid triglycerides and cross-linked at ambient temperatures is disclosed.
64	US 9193862 / 2012	Gehringer, et al. (BASF)	HNIPU on the base of epoxy resins, amine hardeners (0.3-0.9 eqv.), catalyst and monocyclic carbonate for fiber-reinforced cured compositions.
65	US Application 20150024138 / 2013	Figovsky, et al. (Polymate, NTI)	Method for forming a sprayable non-isocyanate foam composition.
66	CA 2876736, 2014	Figovsky, et al. (Polymate, NTI)	Radiation-curable biobased flooring compositions with nonreactive additives (biobased hydroxyurethanes and silane-based hydroxyurethanes).
67	US Application 20150353683, 2014	Birukov, et al. (Polymate, NTI)	A new hybrid epoxy-amine hydroxyurethane network polymers with lengthy epoxy-amine chains and pendulous hydroxyurethane units.

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68	US Application 20150247004 / 2014	Lombardo et al. (Dow Global Technologies)	A method of forming non-isocyanate based polyurethane includes providing a cyclic carbonate, an amine, and a cooperative catalyst system that has a Lewis acid and a Lewis base.
69	WO 015107113 / 2014	Darroman et al. (University of Montpellier, France)	The invention relates to a composition that includes cork or a cork-based material and a binder which includes at least one polyhydroxyurethane prepared using raw materials that are not highly toxic, preferably from biomass.

From Table, we see a high activity of the leading companies in the field of NIPU and HNIPU.

Recently, **BASF** pays serious attention to such areas as synthesis of HNIPU on the base of epoxy-amine compositions and CC with unsaturated bonds (P52, P58) or CC with an electron-withdrawing organic group (P60) or conventional alkylene carbonate (P64). Also there were disclosed syntheses of poly-CC:

– on the base of mono-CC contained acid esters and a polyols (P53);

– by reaction of trioxyalkyl amine with (2-oxo-1,3-dioxolan-4-yl)methyl chloroformate in an aqueous/organic two-phase system (P59);

– by homo- or copolymerization of alkylidene-1,3-dioxolan-2-one monomers (P61).

Water-dispersible, cyclocarbonate-functionalized vinyl copolymer binder and an amine curing agent were described in P50.

Dow discloses the following innovations:

– the poly(hydroxyurethane) compositions made from divinylbenzene dicarbonate and polyamines (P55);

– alternative synthesis of NIPU at ambient temperatures from the reaction of polyaldehydes with carbamate functional polymers using an acid catalyst (P56);

– forming of non-isocyanate based polyurethane from a cyclic carbonate, and an amine, in the presence of cooperative catalyst system that has a Lewis acid and a Lewis base (P68).

Regarding the alternative synthesis (P56), we need to make a few comments:

– preferably the polyaldehyde is prepared by complex hydroformylating process with hydrogen gas, carbon monoxide, and an olefin-containing starting compound;

– the polycarbamates are acrylic carbamate functional polymers with a molecular weight of ~15,000 in the form of ~70% solution in n-butyl acetate;

– isocyanates and phosgene are used on the preliminary stages for preparation of the carbamate functional polymers;

– blocking agents (alcohols) are used for regulation of pot life; as a result an additional allocation of water takes place.

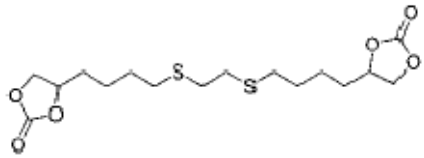
In recent years, companies **Huntsman**, **PPG**, **Rhodia**, **Cognis**, **Henkel**, **Bostic** also received patents in the field of NIPU / HNIPU.

Considerable research work carried out in research centers in Europe, Asia and America. Leading research teams operate in France: Ecole Nationale Supérieure de Chimie / Institut Charles Gerhardt, Montpellier; University of Bordeaux; University of Toulouse; University of Strasbourg; University of Rennes; etc.

In Germany intensive investigations of NIPU are provided in Universities of Freiburg, Aachen, Karlsruhe, etc.

Synthesis of polycarbonate compounds was described in the work [16]. Poly(allyl glycidyl ether) and poly(allyl glycidyl ether-*co*-epichlorohydrin) were prepared by monomer-activated anionic polymerization. Following the same polymerization route, the copolymerization of AGE and epichlorohydrin yields in a living-like manner gradient-type copolymers with controlled molar masses. Chemical modification of the pendant allyl group into cyclic carbonate was then investigated and the corresponding polymers were used as precursors for the isocyanate-free synthesis of polyurethane networks in presence of a diamine.

A new synthesis of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC) was performed by Williamson ether synthesis from 4-(hydroxymethyl)-1,3-dioxolan-2-one [17]. Dicyclocarbonates were synthesized by UV thiol–ene coupling of allyl-cyclocarbonate with a 2,2'-oxydiethanethiol.



This photochemical thiol–ene reaction was carried out under air, with neither solvent nor photoinitiator. The synthesized dicyclocarbonates were used to synthesize polyhydroxyurethanes without isocyanate by step growth polyaddition with 1,10-diaminodecane.

Research group of the Institute Charles Gerhardt, Montpellier, realized for the first time a complete study of the free radical polymerization (FRP) of (2-oxo-1,3-dioxolan-4-yl) methyl methacrylate or glycerin carbonate methacrylate (GCMA) [18]. This methacrylic cyclic carbonate compound allows the synthesis of polymers bearing cyclic carbonate functional groups which can be used for crosslinking reactions in order to form urethane linkages without the use of harmful isocyanates. Transfer reactions to the cyclic carbonate moiety were identified during the polymerization of GCMA. The calculations of the kinetic constants during the copolymerization of GCMA with MMA show the high reactivity of this monomer.

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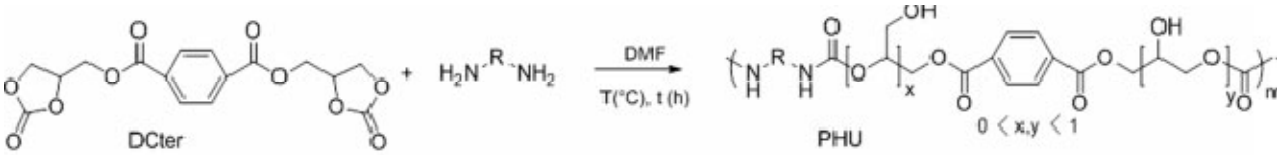
A vinyl ether bearing a carbonate side group (2-oxo-1,3-dioxolan-4-yl-methyl vinyl ether, GCVE) was synthesized and copolymerized with various commercially available fluoroolefins [chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), and perfluoromethyl vinyl ether (PMVE)] by radical copolymerization initiated by tert-butyl peroxypivalate [19]. Although HFP, PMVE, and vinyl ether do not homopolymerize under radical conditions, they copolymerized easily yielding alternating poly(GCVE-alt-F-alkene) copolymers. These original copolymers may find potential interest as polymer electrolytes in lithium ions batteries.

The article [20] focuses on the synthesis and characterization of polyhydroxyurethanes (PHUs) obtained from the reaction between bis[(2-oxo-1,3-dioxolan-4-yl)methyl]benzene-1,4-dicarboxylate (DCter) and various diamines (aliphatic, cycloaliphatic and oligomeric) or polyamines (diethylenetriamine (DETA) and triethylenetetramine (TETA)).



Two different kinds of PHUs were obtained. On the one hand, the use of diamines led to thermoplastic polymers with a glass transition temperature (T_g) ranging from 4 to 78° C depending on the flexibility of the diamine involved in the reaction. On the other hand, PHUs produced from polyamines TETA and DETA were found to be insoluble and infusible due to the creation of polymeric networks. The DCter–DETA polymer had a higher T_g revealing a probable difference in the reactivity of primary and secondary amine groups.

The article [21] describes the synthesis of new cyclic compounds able to react with amines to get NIPUs. The contribution of the most studied five-membered cyclic carbonate was compared to five-membered cyclic dithiocarbonate analogous and to a six-membered cyclic carbonate. Difunctional reactive species were obtained by a simple substitution reaction or an efficient thiol–ene coupling reaction. The dicyclocarbonates were then used to synthesize NIPUs by step growth polymerization with several diamines. Such materials are interesting candidates for coating applications.

Several papers were devoted to the study of the mechanisms of NIPUs preparation.

Polyhydroxyurethanes (PHUs) produced by the reaction between dicyclocarbonate and diamine groups are often presented as possible candidates to substitute for classical polyurethanes based on isocyanate precursors. In the literature, the synthesis of this class of polymers is often performed according to arbitrary conditions of time and temperature without any scientific justification. As such, the real potential of PHUs is probably not fully known. Numerous contradictions in published results seem to support this hypothesis. Authors of the work [22] propose two methodologies based on dynamic rheometry to determine optimized conditions for the synthesis of PHUs. The case of a PHU formed by the reaction between 1,10-diaminodecane and a dicyclocarbonate bearing a central aromatic group is described more precisely. The first approach consists of conducting various rheological experiments (kinetics, thermomechanical analyses) *in situ* on the reaction mixture. The second one retains the same technique to qualify the viscoelastic properties of PHUs synthesized according to various conditions. In this latter case, all samples show thermomechanical behaviour of amorphous thermoplastic polymers. But discrepancies are observed with regard to the value of the glass transition temperature and the existence or not of a rubbery zone. Comparison of these data with size exclusion chromatography results shows that these differences are direct consequences of the polymer molecular weight that can be predicted using macromolecular theory. The properties of the PHUs obtained after optimization of the polymerization reaction were compared with literature data in order to complete the evaluation of the efficiency of the rheological methodology.

Investigation of the reactivity of amine groups in the reaction with cyclic carbonate group was described in the work [23]. The capacity of either primary or secondary amines to open five-membered cyclic carbonates was demonstrated. Thus primary amines react at relatively low temperature (around 70 °C), reachable secondary amines are able to react at temperature a few more elevated (around 90 °C) and less accessible secondary amines (in the middle of the chain) can react only at temperature up to 200 °C.

Catalyzed aminolysis of cyclic carbonates was investigated in work [24]. The work demonstrates that in general, organocatalysts display a higher catalytic activity than inorganic Lewis acids. In addition, they generally do not bring color or turbidity to the reaction mixture. This observation is absolutely crucial for future macromolecular applications. Advantageously, this study has been carried out in the absence of solvent which is also relevant for subsequent extension in polycondensation reactions. The screening also reveals that TBD and the cyclohexylphenyl thiourea A outperform the other catalysts investigated. This observation confirms precedent from the literature. However, in our conditions, the thiourea A seems more promising as it cleanly catalyzes the aminolysis of

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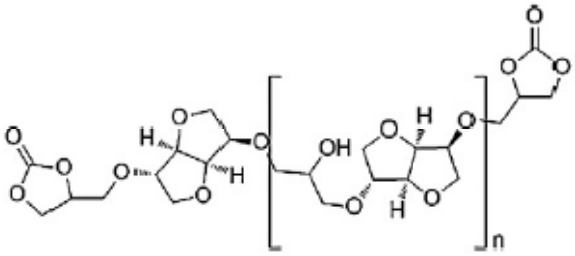
carbonates even at very low catalyst loading. In addition, it was proven more efficient when functionalized 5-membered ring or 6-membered ring carbonates were used.

The mechanism of the reaction of cyclic carbonates with amines, providing non-isocyanate urethanes, was studied by means of quantum chemical calculation in terms of DFT by the PBE/TZ2P method using as examples the reactions of ethylene carbonate and propylene carbonate with methylamine [25, 26]. Structural investigations have revealed four cyclic isomers with intramolecular hydrogen bond and six open conformers.

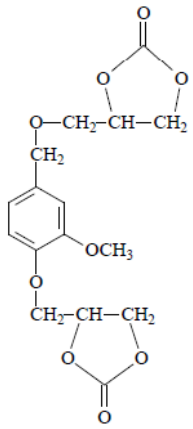
The quantum chemical study of the mechanism of catalysis by acetic acid in the addition reaction of amines with cyclocarbonates showed that the reaction can proceed through both the one step and multistep pathways [27]. The experimental study of the kinetics of the model reaction in the presence of acetic acid confirmed a substantial decrease in the activation energy compared to the noncatalytic process and the reaction involving the second amine molecule as the catalyst.

In recent years, the sustainability is becoming increasingly important for the chemical industry; thus, the use of renewable resources has gained interest in polymer applications [28, 29]. Thiol-ene coupling allows to synthesize new biobased reactants with various function and functionality with reaction conditions in agreement with green chemistry principles: it does not use neither solvent nor initiator or need simple purification step, feasible at industrial scale. Building blocks synthesized have various functions and functionality, including these: dicyclocarbonates and polyamines from vegetable oils and from glycerine derivatives. They were used for the synthesis of biobased polyhydroxyurethanes.

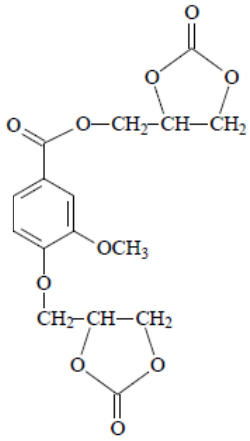
In new developments of the Montpellier's research group were prepared and examined NIPU on the base of isosorbide [30] and vanillin derivatives [31]:



Isosorbidedicyclocarbonate, n ~ 0.5-1.5



Vanillin Bis Carbonate



Vanillic Acid Bis Carbonate

(Bis) 6-membered cyclic carbonates were prepared from methyl 10-undecenoate, which is produced from ricinoleic acid, a main constituent of castor oil [32]. Kinetic studies on these new fatty acid-based 6-membered cyclic carbonates revealed that they are much more reactive than their homologs, 5-membered ones (30 times). Poly(hydroxyurethane)s (PHUs) were then synthesized from these bis 6-membered cyclic carbonates at a temperature as low as room temperature and in the solvent or bulk. Unexpectedly, chemical gels were obtained. The latter were the consequence of side reactions of carbonate ring-opening with the hydroxyl groups of the formed poly(hydroxyurethane)s. Quenching with a large excess of hexylamine enabled the breaking-up of the gel with the formation of urea linkages.

Fatty acid-based bis-cyclic 5-membered carbonates containing amide linkages were prepared from methyl 10-undecenoate [33]. The reaction in bulk of these bio-based carbonates with a series of di-amines led to poly(hydroxyurethane amide)s with molar masses up to 31 000 g mol^{-1}. As expected, the so-formed bio-based thermoplastic poly(hydroxyurethane)s exhibit amorphous to semi-crystalline features with respect to the chemical structure of the monomers used.

The structures of epoxidized and cyclocarbonate-containing natural oligomers were studied [34]. It has shown that they are characterized by an extremely broad composition distribution, reflecting almost the entire range of components contained in natural raw materials. Natural oligomers based on plant oils have a very narrow molecular-mass distribution, and in this respect, they are even simpler than their synthetic analogs.

The synthesis of sustainable NIPU with use of Diels-Alder reaction between the furan-bearing hydroxyurethanes and the bismaleimides was described in the works [35–36].

HNIPUs were synthesized from PolyHydroxyUrethane (PHU) prepolymers terminated amine and epoxy multifunctional resins [37]. These epoxyurethane materials formulated in this study have good thermal properties compared to polyurethane and

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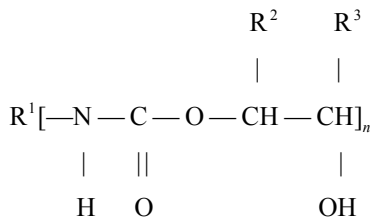
nonisocyanate polyurethane materials. The main advantage of this technology is the ability to obtain PHU materials with a sequence of soft and hard segments as for classic polyurethanes.

Recent elaborations of Polymate Ltd. / Hybrid Coating Technologies / Nanotech Industries: Hydroxyurethane modifiers (HUM)

All known polymer compositions with hydroxyalkyl urethane monomers require specific chemical reactions (such as transetherification, transamination, or self-crosslinking). 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]. The authors recently proposed a novel concept of generating new multifunctional modifiers. The HUM, which possesses a wide range of hydrogen bonds, is embedded in an epoxy polymer network without a direct chemical interaction. Our patent [T1, P48] 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:



wherein R^1 is a residue of the primary amine, R^2 and R^3 are the same or different and are selected from the group consisting of H, alkyl, hydroxyalkyl, and n satisfies the following condition: $n \geq 2$. Diluents, pigments, and additives can be used. The new modifier primarily affects a significant acceleration of the curing process as well as an increase in abrasion resistance.

Doping with the HUM imparts to the cured composition superior coating performance characteristics (pot life/drying, strength-stress properties, bonding to a variety of substrates, appearance in a well-balanced state). Since the structure of the polymer network is not broken, other characteristics, such as weathering and chemical resistance, do not worsen. Use of the modifiers in different structures with varying amounts allows obtaining an epoxy-based coating with tunable hydrogen bonds. It has recently been confirmed by the positive effect of H-bonding moieties into epoxy-amine network. In the work [38] was shown, that the incorporation of acetamide into the covalent networks suggests preemptive healing behavior which helps to reduce the internal stresses arising during the curing of the coating. The fully covalent network and the hydrogen bonded network did not show a pronounced difference in strength under dry conditions and maintain extreme good wet adhesion. Also, the introduction of hydrogen bonds on epoxyamine coatings impart a superior relaxation of the mechanical stresses and promotes flow, at temperatures just below T_g, which assists the self-healing of mechanical damage.

A nanostructured hybrid liquid oligomer composition including at least one epoxy-functional component (A), at least one cyclic carbonate component (B), at least one amine-functional component (C), and, optionally, at least one acrylate (methacrylate) functional component (D), wherein at least one epoxy**,** amine or acrylate (methacrylate) component contains alkoxysilane units was described in patent application [T1, P47]. The composition is highly curable at low temperatures (approximately 10 to 30° C) with forming of nanostructure under the influence of atmospheric moisture and the forming of active, specific hydroxyl groups by reaction of cyclic carbonates with amine functionalities. According to the present invention, the cured composition has excellent strength-stress properties, adhesion to a variety of substrates, appearance, and resistance to weathering, abrasion, and solvents.

Hybrid epoxy-hydroxyurethane compositions cross-linked at ambient temperatures were obtained on the base of renewable raw materials [T1, P63]. In the compositions were used HUMs on the base of carbonated-epoxidized soybean oil and monoamines, without the use of isocyanate intermediates. Compositions can apply to the preparation of curable polymeric foam and other materials (coatings, sealants, adhesives).

A non-isocyanate composite modifier was used in the acrylic radiation-curable composition [T1, 66]. The additive comprises a) a biobased hydroxyurethane additive of formula (1):

$$R^1[-NH-COO-CR^2H-CR^3H(OH)]_2, \qquad (1)$$

wherein R^1 is a residue of the biobased primary diamine, and R^2 and R^3 are the same or different and are selected from the group consisting of H, alkyl, and hydroxyalkyl; and b) a silane-based hydroxyurethane additive of formula (2):

$$(R^6)_{3-n}(OR^5)_n Si-R^4-NH-COO-CR^2H-CR^3H(OH), \qquad (2)$$

wherein R^2 and R^3 are the same as stated above, R^4 is generally an aliphatic group having from 1 to 6 carbon atoms, R^5 and 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.

Recently Polymate Ltd. developed a new hybrid epoxy-amine hydroxyurethane network polymers with lengthy epoxy-amine chains and pendulous hydroxyurethane units [T1, P68]. The cured linear

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hybrid epoxy-amine hydroxyurethane-grafted polymers by novel structure have a controlled number of cross-links and combine increased flexibility with well-balanced physical-mechanical and physical-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.

The schematic structural formula of the novel polymer is the following:

```
...— N — E — R' — E — N — E — R' — E — N — E — R' — E — N — E — R' — E...
     |                |                |                |
     A                A                A                A
     |                |                |                |
     U(OH)            U(OH)            U(OH)            U(OH)
```

where E—R`—E is a residue of a diglycidyl ether, which reacted with amine hydrogens; E is a converted epoxy group, i.e., $–CH_2–CH(OH)–CH_2–O–$; N is a nitrogen atom; A is a residue of a di-primary amine; U(OH) is a hydroxyurethane group,
i.e., $–R^1–NH–CO–O–CH(R^2)–CH(OH)–R^3$, and =N—A—U(OH) is a residue of aminohydroxyurethane with the number of free amine hydrogen atoms equal 2.

A schematic structural formula of the novel polymer with the directions of the possible cross-links (shown by arrows) is the following:

```
                                                                  ↑
                                                                  E
                                                                  |
...— N — E — R' — E — N — E — R' — E — N — E — R' — E — N — E — R" — E...
     |                |                |                |
     A — N →          A                A                A
     |                |                |                |
     U(OH)            U(OH)            U(OH)            U(OH)
```

where $\begin{matrix} E \\ | \\ E — R'' — E \end{matrix}$ 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 also may be used for cross-linking.

Conclusion

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 contained 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, comprised epoxy matrix modified by NIPU, are commercially available under the name Green Polyurethane™ as an isocyanate-free and phosgene-free alternative to conventional materials and represent the first successful application of HNIPUs in the industry. As it was stated by Nanotech Industries, 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.

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