Nonisocyanate hybrid polyurethane floorings based on cyclic carbonates: optimal compositions and service properties

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Abstract. Hybrid nonisocyanate polyurethane (HNIPU) materials are formed by the reaction between adducts of the oligomeric cyclocarbonates with primary di- and polyamines and epoxy oligomers. These materials do not have pores due to the reaction of their formation is insensitive to the moisture of fillers or substrate surface. Chemical resistance of the obtained material containing intramolecular hydrogen bonds is 1.5-2 times greater than material of the same chemical structure but without such bonds. The new material as well as ecologically safe method of its manufacture is discussed. HNIPU materials could be applied for monolithic floor coverings having high chemical-, crack-, wear- and fire resistance and minimal absorption of toxic or radioactive contaminations. The floorings have high adhesion, wear and impact resistance: do not contain organic solvents, harmful and toxic isocyanate substances. Monolithic two-component HNIPU floor coverings are used for manufacture of seamless floors where cleanliness, durability and abrasion resistance are crucial. The optimum composition and operational data of the flooring coverings are discussed.

1. Monolithic flooring based on nonisocyanate polyurethanes binders [1-6]

Modern industrial floors must be appropriate to comply with a great variety of the requirements such as dustless surface, high strength, evenness, high wear resistance, easy cleaning, etc. Durability and chemical resistance of monolithic floor covering depends on properties of a binder. A high build brush or roller applied polyurethane coating for concrete, granolithic, sand / cement and polyester type of a base course allows providing long time stability of monolithic covering and its high crack resistance. It has excellent resistance to attack from spillage of a wide range of contaminants. However hydrolytic stability of existing polyurethanes is quite poor owing to a lot of pores. Other essential lack is process of manufacture of polyurethanes with use of toxic isocyanates.

Nonisocyanate polyurethane materials are formed by the reaction between oligomeric cyclocarbonates and primary di- and polyamines resulting in an increasing of the hydrolytic stability of hetero chain polymers. An intramolecular hydrogen bond is derived from the hydroxyl group at the β-carbon atom of the polyurethane chain as illustrated below:

\[
\text{R-O-CH}_2-\text{CH}_2-\text{CH}_2+\text{HNR} \rightarrow \text{R-O-CH}_2-\text{CH}_2-\text{CH}_2-\text{O-C-NH-R}
\]

\[
\begin{array}{c|c|c}
\text{I} & \text{II} & \text{III} \\
\text{0} & \text{0} & \text{0} \\
\text{OH} & \text{...} & \text{0} \\
\end{array}
\]

(1)
Quantum-mechanical calculation, IR and NMR spectroscopic investigations have confirmed the stability of the resulting product with essentially low hydrolytic activity. The material have not pores because the reaction of its formation is insensitive to the moisture of fillers or substrate surface. Chemical resistance of the obtained material containing intramolecular hydrogen bonds is 1.5-2 times greater than material of the same chemical structure but without such bonds. In this way modifying structure of the polymer, interrelation between structural parameters and properties of the new material and ecologically safe method of its manufacture were elaborate and approved.

Nonylsocyonate polyurethane materials manufacture were elaborate and approved could be homogenous and do not require any solvents at preparation. The main cyclocarbonate oligomers are produced by bubbling the carbon dioxide through epoxy liquid oligomers in the presence of a catalyst. These cyclocarbonate oligomers and primary amine oligomers are used.

Mechanical and operational properties of two-component nonisocyanate polyurethane flooring are illustrated in the Tables 1 and 2. Each test sample includes 150 weight parts (w.p.) of quartz filler per 100w.p of the binder.

**Table 1. Mechanical properties of two-component filled nonisocyanate polyurethane covering**

| Type of cyclocarbonate oligomer | Functionality of cyclocarbonate oligomer | Tensile strength / Elongation, (MPa / %) |
|--------------------------------|----------------------------------------|-------------------------------------|
|                                |                                        | Functionality                        |
| 2                              | I                                      | 1.9/710                             |
| 3                              | I                                      | 8.8/220                             |
| 5                              | I                                      | 21.3/72                             |
| 2.45                           | II                                     | 8.2/315                             |
| 3.1                            | II                                     | 19.3/88                             |
| 3.9                            | II                                     | 19.9/82                             |
| 3.9                            | II                                     | 16.9/73                             |

**Table 2. Basic operational properties of the covering**

| Properties                              | Indices |
|-----------------------------------------|---------|
| Solid, %                                | 100     |
| Pot life (doubling initial viscosity), hours | 2-4     |
| Curing time                             | 4-7 days at 18 - 22°C |
| Film appearance                         | Clear smooth |
| Pencil hardness                         | >2H     |
| Impact, kg*cm                           | 50      |
| Coefficient of chemical resistant:      | 0.90 - 0.95 |
| H₂SO₄, 10% at the 60°C                  | 0.95 -1.0 |
| NaOH, 10% at the 60°C                   | 0.95 -0.90 |
| H₂O, at the 60°C                        |         |

The chemical resistance of nonisocyanate polyurethanes can be increased by adding inorganic powdered substances during the fabrication process. The substances selectively interact with water and aggressive medium (acids, alkalis and salts) by forming a system of high-strength hydrate complexes into durable inorganic adhesive cements. At interaction with the medium crystal hydrates penetrate
into micropores and microcracks of a material. This process "heals" a material and to produce the covering with externally high water and solvent resistance, high adhesion to different substrates.

![Figure 1. Flooring of Triborough Bridge and Tunnel Authority Randall's Island, New York](image)

Advanced way of modification of epoxy polymers is introduction into epoxy matrix hydroxyurethane modifiers (HUM). HUM are prepared by mixing of amines and monocyclocarbonates. Structure of HUM depends on amines and cyclocarbonates. In case of propylene carbonate and diamines we can prepare different urethandiols with different \( \text{–R–} \)

\[
\text{H}_2\text{N–R–NH}_2 \quad \rightarrow \quad \text{2 CH}_3\text{–CH–CH}_2 \rightarrow \\
\begin{array}{c}
\text{H} \\
\text{O}
\end{array}
\]

(2)

If amine \( \text{H}_2\text{N–R–NH}_2 \) contains only primary amino groups HUM has not reactive (for hybrid epoxy-hydroxyurethane systems) functionalities. If amine’s radical \( \text{R} \) contains secondary amino groups too HUM can react with epoxy functionalities. Cyclocarbonate groups can react only with primary amino groups and not with secondary. HUM is compatible with epoxy-amine polymers and is used for their modification.

Structure of the network polymers depends on used HUM. In case of HUM based on primary diamines there are formed clathrates at the expense of hydrogen bonds.

In case of HUM that also contains secondary amino groups, additional covalent chemical bonds are formed.

We have system of pendant hydroxyurethane groups in the epoxy-amine matrix.

The epoxy-amine polymers with HUM are obtained without toxic isocyanates and have increased mechanical properties.

So it is possible to prepare composite materials with advanced properties. All HUM can be easily prepared from cyclocarbonates and amines. The reaction is carried out at 80°C during 1.5-2.0 hours.

The proposed dendro-aminosilane hardeners give the possibility to introduce the siloxane fragments into aromatic structure of diphenylolpropane based epoxy-amine network polymers. Additional hydrolysis of aminosilane oligomer creates the secondary nano-structured network polymer that improves the service properties of the compound. Branched (dendro) polyamine hardeners are novel direction in epoxy and cyclocarbonate and acryl resins chemistry.

The new hardeners give rise to formation of interpenetrating polymer network (IPN) of a polymerized resin with a polysiloxane network by the hydrolytic polycondensation of silane groups. IPN network may be formed on the base of epoxy-cyclocarbonate oligomers. It was found that at least
0.1 equivalent weight of silane per epoxy resin equivalent weight may result in IPN formation. It has been known that epoxy resin has low resistance to acetone and methanol attack. IPN film provides increasing the resistance.

2. **New high quality monolithic flooring ECPU 2851TM (Polymate Ltd.-INRC)**

Monolithic two-component nonisocyanate floor covering ECPU 2851 is elaborated on the base of cyclocarbonate and epoxy oligomers. The covering is destined for manufacture of seamless indoor floors. For areas where both cleanliness and durability are crucial, Flow fresh ECPU 2851 flooring systems deliver absolute reliability. It does not contain organic solvent, harmful and toxic substances, possesses high chemical and abrasive resistance, can be operated in high humidity media, and meets the special sanitary-and-hygienic requirements, ideally suited to industrial, institutional and commercial uses.

The suggested monolithic floor covering can find application in:
- Enterprises of light and food-processing industry, catering;
- Enterprises of chemical, paint-varnish and pharmaceutical industry;
- Enterprises of electronic industry and precise mechanical engineering;
- Enterprises of machine building and aerospace industry;
- Enterprises of wood-working industry;
- Medical institutions and objects of consumer services;
- Trading premises and warehouses;
- Premises with increased decorative requirements: trading and showrooms, television studious etc.

A color glass chips can be inserted in ECPU 2851 flooring with the subsequent covering with the transparent protective varnish. Binder with rubber granules, quartz can be used on ramps and other critical places for increase of adhesion. The coating can be of any color. Figure 2 illustrates recommended structure of the floor covering ECPU 2851.

![Figure 2](image_url)

**Figure 2.** Recommended structure of the floor covering ECPU 2851: 1 - substrate; 2 - primer; 3 - covering ECPU 2851 with thickness 0.5-3mm

The properties of such hybrid nonisocyanate polyurethane covering are given at Tables 3-5.

| Properties                                      | Indices                      |
|------------------------------------------------|------------------------------|
| Coating material                               | Two-component hybrid nonisocyanate polyurethane |
| Ratio of components on weight (binder : hardener) | 100 : 55                     |

Table 3. Properties of the hybrid nonisocyanate polyurethane floor covering ECPU 2851
Viscosity of binder: No more 3000 cps at 25°C (Brookfield RVDV I Spindle 29, velocity 100 rpm1)

| Property          | Value                          |
|-------------------|--------------------------------|
| Standard colors   | According to catalog of basic colors |
| Pot life          | 40-60 min at 25°C               |
| Substrate         | Concrete, cement cover, a cover, asphalt, wood, etc. |

| Property         | Value                          |
|------------------|--------------------------------|
| Primer           | Depends on substrate           |
| Thickness of the coating | 0.5-3mm                     |
| Application temperature | 15-25°C                    |
| Curing time      | Walk-on in 24h. at 25°C, full chemical load: 7 to 10 days |

Table 4. Mechanical properties of the hybrid nonisocyanate polyurethane floor covering ECPU 2851 (after 10 days at 25°C)

| Properties                  | Indices                          |
|-----------------------------|----------------------------------|
| Rupture strength            | 3-4 kg/mm²                       |
| Elongation at rupture       | 4.8%                             |
| Hardness (Shore D)          | More than 72                     |
| Wear resistance (ASTM 4060-90) | 70-100mg/1000cycles             |
|                             | (Taber CS-17 wheel, 1000g weight) |

Table 5. Chemical properties of the hybrid nonisocyanate polyurethane floor covering ECPU 2851 (after 14 days at 25°C)

| Media          | Resistance                     |
|----------------|--------------------------------|
| Water          |                                |
| Petrol         |                                |
| Aviation petrol|                                |
| Oil            |                                |
| NaCl (5%)      |                                |
| Formaldehyde   | Resistant during short time    |
| Sulfuric acid (20%) |                            |
| NaOH (20%)     |                                |
| Benzene        |                                |
| Alcohols       | Not Resistant                  |

3. On optimization of a monolithic polymer chemical resistant flooring [7,8]

Depending on operating conditions the requirements to the polymeric floor composition of industrial building are quite varied and therefore in construction practice a plenty of various types and functions coverings are applied. In this connection the optimization problem of materials forming specific layers of floor covering is actual. A mathematical model of optimal monolithic covering is suggested. The
model can be realized in multifactor space of specific manufacture conditions $d_i$, including among other the indices of durability, labor-intensiveness and cost.

Efficiency function of such model looks like:

$$D = (1d_i)^{1/n}$$

where: $D$ – generalized optimization criterion; $d_i$ is the individual optimization factor determined by the formula:

$$d_i = \exp[-\exp(y'_i)] ; \ 0 < d_i < 1$$

and $y'_i$ is scale of the $i$- factor (usually $-3 < y'_1, 3$ in all of the range $y_i$).

Here

$$y_i = f(x_1, x_2, ..., x_n, z_1, z_2, ..., z_k, t)$$

where $y_i$ – “weight” characteristic $i$-th parameter; $x_1, x_2, ..., x_n$ – quantity of the given component in the composition; $z_1, z_2, ..., z_k$ - operating conditions during time $t$.

Substitution of Eq.5 into Eqs.3 and 4 makes possible to find the efficiency function $D$ in the all factorial space $x_n$ at interval $\Delta t$ at fixed operating conditions $z_k$.

A triaxial stress-strain state arises in a floor covering during its shrinkage. However one can consider that plane stress-strain state occurs in the central part of the covering. At unrestrained (free) shrinkage the mechanical properties of the covering is changed as it hardening.

The stress-strain state of “optimal” monolithic floor covering is calculated on the base viscous-elastic rheology Maxwell model of non-linear continuum as applied to inner stresses at a covering curing. On the assumption that all model parameters are differentiable with respect to time the normal tension stress is obtained:

$$\frac{d\sigma}{dt} = \sigma \left[ \frac{1}{T} - \frac{1}{E \frac{d\varepsilon}{dt}} \right] = E \left( \frac{d\varepsilon}{dt} \right)$$

where $\sigma = \sigma(t)$, $\varepsilon = \varepsilon(t)$, $E=\varepsilon(t)$, $T=\mu/E = T(t)$, $\mu= \mu(t)$ are tension stress, elongation, modulus of elasticity, and Poisson’s ratio as functions of time, respectively

The solution of Eq.5 is: Eq.6:

$$\sigma = \exp \left[ \int_0^t \left( \frac{1}{T} - \frac{1}{E \frac{d\varepsilon}{dt}} \right) dt \right] \left[ \int_0^t E \frac{d\varepsilon}{dt} \left( \frac{1}{T} - \frac{1}{E \frac{d\varepsilon}{dt}} \right) dt \right] + \varepsilon_i$$

where constant $T$ is found from the initial conditions ($\sigma =0$ for $t =0$)

Experimental dependences of the modulus of elasticity, viscosity and deformation of free shrinkage on time were determined for the most materials that are used for seamless polymer floors. These dependences can be described by the following hyperbolic functions with accuracy that is sufficient for practical calculations:

$$\varepsilon = \varepsilon_\infty \text{th} \ kt; \ E=\varepsilon_\infty \text{th}^m \ kt; \ \mu= \mu_1 \text{[th} \ kt (1-p \text{th} \ kt)] / 1\text{-th}^2 \ kt \ \ \ \ T= \text{T}_1 (1-p \text{th} \ kt) / 1\text{-th}^2 \ kt,$$

where $\varepsilon_\infty$ and $E_\infty$ are the limiting values of residual deformation and modulus of elasticity of the material at free shrinkage respectively ($t \rightarrow \infty$) ; $m, p, k$ are the constants of the material. It should be noted that for purely elastic materials in hardened state $0 < p < 1$ and $\mu \rightarrow \infty$ at $t \rightarrow \infty$; for viscoelastic compositions in hardened state $p=1, T_1 \rightarrow \infty$. 
Substitution of Eq. 8 in Eq. 9.5 gives:

\[
\sigma = \left[ \sigma_\infty (1 - p \text{ th} \ kt) \text{ th}^m kt \right] / q - p, \tag{9}
\]

where \( \sigma_\infty, E_\infty, \epsilon_{\text{nom}} \) — nominal stress; \( q = 1 / T_1 \)

Results of experiments with sufficient accuracy have coincided with calculated ones. Thus the deduced interrelation between separate parameters of curing stress allows changing the properties of a composition for produce the floor covering with beforehand given properties. Recommendation for design impact- and chemical- resistant covering with application the specific inorganic additives, which form the high strength hydrate complexes with aggressive environment, are given.

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