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FUNCTIONAL POLYURETHANE COATINGS FOR PROTECTION OF DIFFERENT SURFACES FROM AGGRESSIVE ENVIRONMENTAL FACTORS

New polyurethane composites (PCs) have been created. They are multifunctional protective materials used as coatings, binders or impregnating materials. The PCs have high adhesion values. The PC-based materials are waterproof and resistant to aggressive biotic (abiotic) and anthropogenic factors (bio-corrosion, UV radiation, chemical agents). Being imbedded in polymer macro-chain the active compounds prolong the action of protective mechanisms of proposed materials thereby giving them an advantage over the existing substances.

Key words: polyurethane coating, protection, multi-functionality, biotic (abiotic) and anthropogenic factors, and stability.

Among the urgent problems to be addressed in the field of construction, architecture, preservation of architectural and historical monuments, housing, utilities, transportation, chemical and food industries, there is the creation of new, more efficient, durable, and economical composite materials with improved properties of multifunctional coatings and impregnating materials in order to extend the operating life of new and old buildings and structures [1].

Currently, the stability of materials and structures exposed to harsh environmental factors is defined in terms of two research areas: the chemical and the biological ones. The chemical aspects of material degradation are widely known. They are the abiotic and the anthropogenic factors. The reliability and durability of materials, buildings, facilities, and structures destroyed by microorganisms is an actual problem of growing importance. According to the recent inventory the list of microorganisms that are bio-destructors of polymeric, metallic, and non-metallic (stone, concrete, granite, and wood) materials includes more than 360 species, among which the most aggressive are *Aspergillus* and *Penicilium* fungi [2]. In addition, populations of new extremely aggressive bio-destructors have appeared under the influence of extreme factors (including the environmental ones).

Addressing the protection of buildings and structures from decay under the influence of destructive environmental factors is possible with the use of polyurethane composites (PCs) as a multifunctional coating and impregnating material. They are created on their basis of innovative protection technologies. The polyurethanes should be considered not only as a class of polymers, but also as a successful and efficient way to create effective polymers with targeted structure and properties [3]. This property of high-molecular compounds is based on the fact that the polyurethane elastomers are block copolymers of $[ABC]_n$ type obtained from reactive reagents of different classes of organic compounds, which makes it possible to vary controllably the structure and properties of polymer macromolecules. The key problem of the creation of composite materials is related to the interaction between the components and their influence on the composite structure. The modification of polymers by chelate complexes of transition metals (e.g., zinc, nickel, and copper) provides polymers with ability to counteract the destructive processes based on the hydroperoxide homolysis mechanism (UV and thermal oxidation) [4].

This allows the material engineers to obtain a polymer coating resistant to abiotic and anthropogenic factors. The creation of polymeric materials resistant to bio-corrosion is based on the principles of designing a macromolecule by introducing into its architecture the elements and fragments whose cooperative action induces biological activity, as well as on the targeted choice of modifiers capable of chemical or physical interaction with macro-chain fragments.

Unlike the traditional technologies that offer major repair or replacement of damaged structures and facilities, the technique of repair with the use of protective PC (created as described above) as multifunctional coating and impregnating material will make it possible to repair damaged concrete, reinforced concrete, granite, and other structures; to ensure the operation of buildings, facilities, and metal structures under conditions of dynamic abiotic and anthropogenic stresses; and to guarantee prolonged use of facilities after repair works. This demonstrates the great advantage of these materials over many similar foreign- and domestic-made products. In addition, the developed method allows the researchers and material engineers to obtain composites with targeted properties by functionalization of polymer matrix, as well as by targeted use of modifiers to meet the customer requirements.

As of today, the polymer composites used to protect different types of surfaces [5] have good adhesive and cohesive strength and elasticity. However, they do not possess sufficient resistance to chemical agents, are nonresistant to UV radiation and bio-corrosion, therefore, they cannot ensure the protection against aggressive environmental factors.

Given the above said, we set the goal to develop a multifunctional PC as coating and impregnating material for protection of buildings, structures, different types of surfaces from decay or fracture under the influence of biotic, abiotic, and anthropogenic destructive environmental factors. The proposed PC must have high adhesion, water resistance, heat resistance, as well as resistance to bio-corrosion, UV radiation, and chemical agents and must preserve the technological properties of structures, including their stability and durability.

THE EXPERIMENT

Polyurethane composite used as protective coating is synthesized by reaction of 2,4 (2,6)- toluene diisocyanate and organometallic compound as reactive organometallic modifier (ROM): Ni-organometallic compound (Ni_xL_y), Cu-organometallic compound (Cu_xL_y) or a mixture of Ni-organometallic and Cu-organometallic modifiers (Ni_xL_y+Cu_xL_y) with different molar ratios and with extending the chain by polyoxypropylene glycol MM1000 and mixing in ethyl acetate with branched pre-polymer based on toluene diisocyanate and trimethylolpropane (samples 1, 3, 5, 7, and 10) or linear polyisocyanate (PIC) (samples 2, 4, 6, 8, 9, 11). Samples 10 and 11 as comparison ones are obtained by a similar method, but they do not contain any reactive organometallic modifier.

The PC tests with respect to the impact of complex weather conditions (UV and IR radiation (sunlight), elevated temperature (50 ± 5 °C), and humidity (96%)) have been carried out in a climate chamber during 120 hours, which is an equivalent of 1-year operation under atmospheric conditions.

The PC resistance to bio-corrosion (fungi impact) related to the effect of the most active biodestructors *Aspergillis*, *Penicillium* and other mold fungi was assessed on the basis of fungal growth on PC samples by methods of experimental mycology, in accordance with the results of [6—8]. The PC viability was determined visually by everyday surveillance until the gelation. To do this, the PC samples containing different reactive organometallic modifiers in amount of 120—130 ml of composite were placed in a dark chemical vessel with sealing plugs having a capacity of 150 ml.

The thermal stability of PC film samples was determined by thermogravimetry (using a derivatograph Q-1000 MOM, Hungary). The temperature at which the sample lost 1 wt. % was deemed to be a temperature of degradation start. The

Table 1

Influence of Complex Environmental Factor on PCs

PC	ROM	Physical and mechanical properties			
		Cohesive strength (original sample)		Cohesive strength (after climatic chamber)	
		σ, MPa	ε, %	σ, MPa	ε, %
1	Ni_xL_y	41.5	40	41.0	40
2	Ni_xL_y	37.0	60	37.0	60
3	Cu_xL_y	42.9	40	39.1	30
4	Cu_xL_y	38.2	50	30.1	30
5	Cu_xL_y	42.5	40	38.6	25
6	Cu_xL_y	36.1	64	30.5	30
7	$Ni_xL_y + Cu_xL_y$	46.0	50	46.0	50
8	$Ni_xL_y + Cu_xL_y$	43.5	60	43.6	58
9	$Ni_xL_y + Cu_xL_y$	50.0	59	53.1	50
10	—	40.0	10	30.0	7.3
11	—	20.0	350	10.8	180

Table 2

PC Resistance to Bio-Corrosion (Fungi)

PC	ROM	Effect of bio-destructors			
		Original samples	Humid chamber	Culture medium without contagion	Culture medium with contagion
1	Ni_xL_y	1	1	1	1
2	Ni_xL_y	1	1	1	1
3	Cu_xL_y	0	0	0	0
4	Cu_xL_y	0	0	0	0
5	Cu_xL_y	0	0	0	0
6	Cu_xL_y	0	0	0	0
7	$Ni_xL_y+Cu_xL_y$	0	0	0	0
8	$Ni_xL_y +Cu_xL_y$	0	0	0	0
9	$Ni_xL_y +Cu_xL_y$	0	0	0	0
10	—	1	1	1	2
11	—	1	1	1	2

physical and mechanical properties such as adhesion strength were measured on a tensile machine FU-1000 (VEB MWK *Fritz Heckert*, Germany) beyond the break point by the pull-off method according to [9], while the cohesive properties were determined beyond the ultimate tensile strength σ; the relative elongation ε was calculated according to [10].

The measured values of indicators were reproduced in more than 5 parallel tests. The adhesive

Table 3

Original PC Properties

PC	ROM	Physical and mechanical properties				Thermal stability. °C	Viability. months
		Adhesive strength. σ. MPa		Cohesive strength			
		Original PC. steel-steel. 30 days	After exposure to water steel-steel. 30 days	σ. MPa	ε. %		
1	Ni_xL_y	33.6	32.5	41.5	40	250	≥10
2	Ni_xL_y	20.8	18.2	37.0	60	232	≥10
3	Cu_xL_y	35.0	32.5	42.9	40	260	≥10
4	Cu_xL_y	20.3	17.9	38.2	50	240	≥10
5	Cu_xL_y	35.0	32.5	42.5	40	260	≥10
6	Cu_xL_y	20.1	17.5	36.1	61	230	≥10
7	$Ni_xL_y + Cu_xL_y$	36.0	32.4	46.0	50	265	≥10
8	$Ni_xL_y + Cu_xL_y$	24.5	22.5	43.5	58	270	≥10
9	$Ni_xL_y + Cu_xL_y$	36.6	26.7	50.0	50	270	≥10
10	—	30.0	28.0	40.0	10	180	10
11	—	17.0	14.0	20.0	350	175	10

Table 4

PC Properties after the Action of Bio-Destructors (Resistance to Fungi)

PC	ROM	Physical and mechanical properties after exposure to bio-destructors				Thermal stability, °C	Viability, months
		Adhesive strength, σ, MPa		Cohesive strength			
		Original PC, steel-steel, 30 days	After exposure to water steel-steel, 30 days	σ, MPa	ε, %		
1	Ni_xL_y	33.6	32.5	41.5	40	255	≥10
2	Ni_xL_y	20.8	18.2	37.0	60	232	≥10
3	Cu_xL_y	35.0	32.5	42.9	40	260	≥10
4	Cu_xL_y	20.3	17.9	38.2	50	240	≥10
5	Cu_xL_y	35.0	32.5	42.5	40	260	≥10
6	Cu_xL_y	20.1	17.5	36.1	61	230	≥10
7	$Ni_xL_y + Cu_xL_y$	36.0	32.4	46.0	50	265	≥10
8	$Ni_xL_y + Cu_xL_y$	24.5	22.5	43.5	58	270	≥10
9	$Ni_xL_y + Cu_xL_y$	36.6	26.7	50.0	50	270	≥10
10	—	30.0	28.0	40.0	10	175	10
11	—	17.0	14.0	20.0	350	180	10

properties were studied using cylindrical samples having a diameter of 50 mm and made of GOST-certified steel. A PC drop was placed between two steel samples that were grinded and left upright for 30 days. The PC film samples containing ROM for determining cohesive properties were obtained as follows: a polyurethane solution sample was poured into a plastic mold dried 24 hours in oven at a temperature of 40 °C, degassed during 5 hours under vacuum at a temperature of 30 °C and kept 24–48 hours at room temperature. The sample physical and mechanical properties were measured using the initial PC samples, the PC samples exposed to the action of myco-destructors (molds) and the PC samples tested in the climatic chamber.

Resistance to water, gasoline (diesel), and chemical environments (sulfuric, hydrochloric, and nitric acids) was determined according to the technique described in [11].

RESULTS AND DISCUSSION

The results of studying the effect of complex weather conditions (UV and IR radiation (sunlight), elevated temperature (50 ± 5 °C), and humidity (96%)) on PCs are given in Table 1. It has been established that the samples containing in the PC structure a Ni-organometallic modifier (Ni_xL_y) and a mixture of Ni- and Cu-organometallic modifiers (Ni_xL_y + Cu_xL_y) are resistant to UV and IR radiation, whereas the initial samples and the samples containing a Cu-organometallic modifier (Cu_xL_y) slightly lose their strength and change their color.

The results of the study of resistance to bio-corrosion (funginertness) are showed in Table 2. Before studying the control samples (10, 11) and the samples containing ROM (Ni_xL_y) (1, 2) one colony of spore-bearing myco-destructors (molds) having a diameter of up to 1–2 mm was found on each sample. From these colonies *Penicilium cyclopium* was extracted and identified. No molds were found on the PC samples containing ROM Cu_xL_y and mixture (Ni_xL_y+Cu_xL_y) before the study (Table 2).

It has been established that all the PC samples containing ROM (Cu_xL_y and (Ni_xL_y + Cu_xL_y)) have fungicidal properties. The sample resistance to fungi is 0 points in humidity cabinet, on the culture medium without additional infection and on the culture medium with infection. No increase in the colony has been observed in the PC

Table 5

PC Resistance to Chemical Agents

PC	ROM	Increase in PC sample weight after being exposed to the action of chemical reagents during 240 hours									
		Water	Motor oil	Petrol	Diesel fuel	Ethyl acetate	Benzene	20% solution HCl	20% solution H_2SO_4	20% solution HNO_3	20% solution NaOH
1	Ni_xL_y	1.0	1.16	0.5	4.0	0.9	1.1	1.0	0.8	17.7	0.5
2	Ni_xL_y	1.5	2.1	2.1	5.0	4.0	4.4	8.1	1.0	23.1	0.6
3	Cu_xL_y	1.47	1.1	0.6	4.9	0.9	1.2	1.5	0.6	21.8	0.67
4	Cu_xL_y	0.58	2.5	2.75	5.3	4.5	3.0	6.4	1.4	9.8	0.7
5	Cu_xL_y	1.5	1.2	0.6	4.2	1.65	3.3	1.0	1.0	23.0	0.5
6	Cu_xL_y	1.1	1.2	2.85	1.2	4.0	4.4	5.5	0.85	22.0	0.9
7	Ni_xL_y + Cu_xL_y	1.1	1.3	0.56	3.0	4.0	4.0	1.1	1.1	25.0	0.9
8	Ni_xL_y + Cu_xL_y	1.48	1.1	2.5	3.0	4.0	4.0	1.6	1.14	17.0	0.9
9	Ni_xL_y + Cu_xL_y	1.5	0.7	2.56	3.0	4.0	4.1	2.2	1.15	16.0	0.85
10	–	1.03	0.57	0.5	5.85	7.0	1.1	1.0	1.1	6.4	0.5
11	–	1.6	4.1	5.6	12.0	7.0	4.6	18.5	1.1	16.6	0.85

samples containing ROM Ni_xL_y, although the fungi remained viable until the end of experiment, i.e. the PCs modified by ROM Ni_xL_y have fungistatic properties. An increase in the colony was reported in the control samples (Table 2).

Tables 3 and 4 show the results of studies of the physical and mechanical properties of the initial samples and the PC samples exposed to bio-destructors. As one can see, the samples modified by ROM Cu_xL_y and by (Ni_xL_y + Cu_xL_y) have fungicidal properties, while those modified by ROM Ni_xL_y acquire fungistatic properties.

The synthesized multifunctional PCs were tested with respect to their resistance to chemical environments (Table 5). It has been established that the obtained composites are resistant to water, oil, petrol, diesel fuel, organic solvents, dilute acids, and alkalis.

The study of PCs in natural conditions has showed that all the experimental samples passed the test: the polymer coating surface on all the samples was not damaged, their color and appearance did not change, the coating material did not peel from the sample, while the reverse side of metal plates not protected with polymeric material was covered with a layer of rust (see Figure).

CONCLUSIONS

PCs to be used as multifunctional protective material, coating, impregnating or binding compounds have been created. They have high level of adhesion. The materials based on them are waterproof and resistant to aggressive biotic factors (fungi, ultraviolet irradiation, and chemical agents). The PC samples that do not contain some kind of reactive organometallic modifier do not possess such qualities.

Embedding of active compounds in polymer macro-chain prevents their diffusion to the surface of material and removal thereby prolonging the protective function of coating, which is an advantage of PCs as compared with similar materials of foreign and domestic production.

The polyurethane composites are characterized by stability of their properties and high viability of their solutions (at least, 10 months). The created PCs are protected by five patents of Ukraine.

The way of using polyurethane composites as protective coating is determined by operating conditions: in the case of prevailing biological effects the coatings containing organometallic Cu-modifier apply. In the case of heavy sun exposure the Ni-containing polyurethane composites are used. The best option is the PCs having both Ni- and Cu-organometallic modifiers simultaneously.

The created PCs are recommended for applying as protective, impregnating or binding materials to construction sites, architectural, housing, and infrastructure facilities, in chemical and food industries.

Among the technical and economic advantages of created protective materials there are the infusion of sustainable operational properties and the extension of maintenance-free service life of metal, wood, brick, and concrete structures and buildings. Excellent resistant qualities of polyurethane composite materials and complete conversion of initial reactants make the use of PCs feasible.

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ПОЛИУРЕТАНОВЫЕ ФУНКЦИОНАЛЬНЫЕ ПОКРЫТИЯ ДЛЯ ЗАЩИТЫ РАЗНОГО ТИПА ПОВЕРХНОСТЕЙ ОТ ВОЗДЕЙСТВИЯ АГРЕССИВНЫХ ФАКТОРОВ ВНЕШНЕЙ СРЕДЫ

Созданы полиуретановые композиции как полифункциональные защитные материалы, которые могут выполнять функции покрытий, пропиточных или связующих материалов. Полиуретановые композиции имеют высокие показатели адгезии, а материалы на их основе являются водостойкими и стойкими к воздействию агрессивных биотических (абиотических) и техногенных факторов (биокоррозии, УФ-облучения, химических агентов). Встраивание активных соединений в макроцепь полимера способствует пролонгированию защитных функций предлагаемых материалов, что является их преимуществом над уже существующими.

Ключевые слова: полиуретановое покрытие, защита, полифункциональность, биотические, абиотические и техногенные факторы, стойкость.

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ПОЛІУРЕТАНОВІ ФУНКЦІОНАЛЬНІ ПОКРИТТЯ ДЛЯ ЗАХИСТУ РІЗНОГО ТИПУ ПОВЕРХОНЬ ВІД ДІЇ АГРЕСИВНИХ ФАКТОРІВ ДОВКІЛЛЯ

Створено поліуретанові композиції як поліфункціональні захисні матеріали, що можуть виконувати функції покриттів та просочувальних або зв'язуючих матеріалів. Поліуретанові композиції мають високі показники адгезії, а матеріали на їх основі є водостійкими та стійкими до дії агресивних біотичних (абіотичних) і техногенних факторів (біокорозії, УФ-опромінення, хімічних агентів). Вбудовування активних сполук у макроланцюг полімера сприяє пролонгації захисних функцій пропонованих матеріалів, що є їх перевагою перед уже існуючими.

Ключові слова: поліуретанове покриття, захист, поліфункціональність, біотичні, абіотичні та техногенні фактори, стійкість.

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