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ANTIMICROBIAL HYBRID COATINGS MANUFACTURED BASED ON NOVEL COMPOUNDS WITH SPECIFIC BIOACTIVITY

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ანტიმიკრობული ჰიბრიდული დამცავი საფრები სპეციფიკური ბიოლოგიური აქტიურობის მქონე ნაერთების ბაზაზე

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ივ. ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი

რეზიუმე

ადამიანის ჯანმრთელობის, ასევე კულტურული მემკვიდრეობისა და სამუზეუმო ექსპონატების დაცვის მიზნით მიღებული და შესწავლილი იქნა ახალი ჰიბრიდული ანტიმიკრობული საფრები სილიციუმორგანული პოლიფუნქციური ოლიგომერებით მოდიფიცირებული ზოგიერთი ჰეტეროჯაჭვური პოლიურეთანისა და ერთდროულად ზოგიერთი ბიოგენური ელემენტის, ბის-(η^5-ციკლოპენტადიენილ)რკინის და პოლიფუნქციური ასიმეტრიული ფრაგმენტის შემცველი კოორდინაციული ნაერთების, ასევე მაკროდისპერსიული ბიოაქტიური არაორგანული ნაერთების ბაზაზე. შესწავლილია მიღებული მასალების ძირითადი თერმოფიზიკური დამახასიათებლები. თერმოგრავიმეტრიული ანალიზით დადგენილია, რომ საექსპლუატაციოდ მიღებული არაორგანულ-ორგანული ჰიბრიდები 200^{0}C-მდე საკმაოდ სტაბილურია; დიფერენციულ-მასკანირებელი კალორიმეტრიული (DSC) მეთოდის გამოყენებით დადგინდა, რომ გამინების ტემპერატურული დიაპაზონი ყველა ტესტირებული საფარისათვის +50^{0}C-ზე ზემოთ მდებარეობს. ნაჩვენებია, რომ პოლიმერული მატრიცების სილიციუმორგანული ოლიგომერებით მოდიფიკაცია გამინების ტემპერატურის გარკვეულწილად შემცირებას იწვევს. შესწავლილია შემუშავებული ჰიბრიდული საფარის ზოგიერთი საექსპლუატაციო მახასიათებელი (იზოთერმული დაბერება, შუქ-ამინდისადმი მდგრადობა, ფოტოქიმიური სტაბილურობა, წყალშთანთქმისუნარიანობა).

INTRODUCTION. The aggressive microorganisms and viruses have adverse effects on the environment and human together with three global dangers for humanity: an energy crisis, food crisis and ecological disasters [1]. The growing population of various aggressive micro-organisms stimulates a series of biocorrosive processes that affects many fields of industries and techniques [2]. At present the intensive development of technique and industry makes actual the creation of multifunctional composite materials with antimicrobial properties by various purposes. Hybrid inorganic-organic materials as main components comprises bioactive compounds and polymeric matrices and will play a major role in the development of advanced functional materials that synergistically combine and enhance their best properties [3, 4]. The potential application fields of such hybrids can include specialty coatings, membranes, sensors, drug delivery systems, biomaterials, catalysts etc.

GENERAL RESULTS. In order to create novel inorganic-organic hybrids with specific combinations of properties, stable towards biocorrosion we proposed in perspective the elaboration of non-traditional materials by combining different molecular building blocks in various ratios by controlling their mutual arrangement.

As a bioactive components were used heterometal coordination compounds of some biogenic elements and ligands containing bis(η^5-cyclopentadienyl)iron and polyfunctional asymmetric fragment simultaneously [5]; also compounds obtained by transformation of the raw materials of arsenic chemical plants of Georgian region. These compounds with high probability must display completely new potential of action, typical for combined structures, the ability of suppressing action of various aggressive microorganisms in condition of long-term consumption [6].

The use of silicon-organic oligomers with side functional groups, characterized with a good compatibility as modifiers of existing film-forming adhesive polyurethane matrices (obtained based on 4,4-dimethylmethanediisocianate and oligobuthyleneglicoladipinate) leads to the development of a principally new generation multifunctional antimicrobial coatings with good thermal stability, hydrophobicity and mechanical properties [7]. That gives new opportunities for expansion of their application areas. The optimal ratio of polymers, modifiers and bioactive components were determined.

The work temperature interval of the obtained composites was established by investigation of thermo physical properties. TGA results of PU matrices and hybrids based on them show that up to 200^{0}C they are quite stable and weight loss not exceeds 5-6 wt%. Intensive destruction of all samples takes place above 300-350^{o}C where their total weight loss consists more than 45 wt%; the full thermal degradation of the tested composites takes place above of 600^{0}C.

Differential scanning calorimetric method were used to locate the phase and glass transitions. For DSC measurements were used DSC 200 apparatus from Netzsch, Selb, Germany. Samples of about 10 mg were enclosed in aluminum DSC capsules. All tests were conducted under dry nitrogen in the temperature range from -100^{o}C up to +300^{o}C at a heating rate of 5^{o}C/min.

The analyses of DSC curves show that endothermic picks correspond to the glass transition temperatures of the tested samples (T_g). All obtained coatings have glass transition regions above +50^{o}C. It was established, that the modification of chosen matrices with silicon-organic oligomers causes decrease of glass transition temperatures compared with non-modified polyurethane. Besides obtained coatings are amorphous substances at room temperature (usual temperature for using of the antimicrobial coatings as protectors of museum exhibits) what is very important as crystallization can be worsening their optical properties.

The studies of main operational characteristics show that obtained hybrid coatings:

- are characterized by a good adhesion on surfaces of various synthetic and natural materials;
- do not violate wholeness of samples during hardening and exploiting of the coating composites;
- are transparent and almost do not change the color during their aging (40-60^{o}C in the air);
- have enough strength, elasticity and stable mechanical characteristics, - they do not scratch easily and maintain surface homogeneity without of splits formation;
- are characterized with high hydrophobicity: water absorption ability (W_{H2O}) does not exceed 0.03 wt%, - typical for such materials. W_{H2O} of tested composites depends on the content of silicon-organic modifier and decreases with increasing of modifier concentration;
- are not dangerous for human; during the exploitation they do not produce harmful gases;
- are relatively cheap and available.

By preliminary investigation it was established, that the obtained antimicrobial inorganic-organic hybrid materials may be used for effective protection of cultural heritage and museum exhibits from the action of various aggressive microorganisms what at the same time will provide improving of ecologically and epidemiologically dangerous situation in the environment provoked by the growth and settling of detrimental microorganisms on surfaces of various materials.

CONCLUSION. Based on various bioactive compounds, containing bis(η^5-cyclopentadienyl)iron, polyfunctional organic fragment and some of transition metals simultaneously, also macro dispersed bioactive inorganic compounds and polymeric matrices modified with silicon-organic oligomers the photo-, thermal aging and moisture resistant, with "*Short-time*" antimicrobial active inorganic-organic hybrid multifunctional materials, stable towards the action of various aggressive microorganisms have been created. The obtained composites are optically transparent, smooth and visually homogenous and are characterized with good adhesion on various surfaces. The main thermo physical and operational properties of the obtained composites have been studied by TGA and DSC analyses methods. It has been shown that the proper combination of the structure, bioactivity, ratio of basic components of antimicrobial composites and materials could improve their mechanical, thermal and operational properties. The potential application spheres of obtained bioactive coatings have been established.

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ПРОИЗВОДСТВО АНТИМИКРОБНЫХ ГИБРИДНЫХ ПОКРЫТИЙ НА ОСНОВЕ НОВЫХ СОЕДИНЕНИЙ С УДЕЛЬНОЙ БИОАКТИВНОСТЬЮ

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РЕЗЮМЕ

Новые гибридные антимикробные покрытия на основе некоторых гетероцепных полиуретанов, модифицированных кремнийорганическими полифункциональными олигомерами и координационными соединениями, содержащими бис (η5-циклопентади¬нил) железо, полифункциональный асимметричный фрагмент и одновременно были получены и исследованы некоторые биогенные элементы, а также

макродисперсные биоактивные неорганические соединения с целью защиты здоровья человека, культурного наследия и музейных экспонатов. Изучены основные теплофизические и эксплуатационные характеристики полученных материалов. Путем термогравиметрического анализа установлено, что до 200°С полученные неорганико-органические гибриды достаточно стабильны; с помощью метода дифференциальной сканирующей калориметрии (ДСК) установлено, что области стеклования для всех испытанных покрытий находятся выше + 50°С. Показано, что модификация полимерных матриц кремнийорганическими олигомерами вызывает в некоторой степени снижение температур стеклования. Были изучены некоторые эксплуатационные характеристики (изотермическое старение, погодные условия, фотохимическая стабильность, водопоглощение) разработанных гибридных покрытий.

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SUMMARY

Novel hybrid antimicrobial coatings based on some heterochain polyurethanes modified by silicon organic polyfunctional oligomers and coordination compounds containing bis(η^5-cyclopentadienyl)iron, polyfunctional asymmetric fragment and some biogenic elements simultaneously, also macro dispersed bioactive inorganic compounds have been obtained and studied for purpose of protection of human's health, cultural heritage and museum exhibits. The main thermo physical and operational characteristics of the obtained materials have been studied. By thermogravimetric analysis has been established that up to 200°C obtained inorganic-organic hybrids are quite stable; by using of differential scanning calorimetric (DSC) method have been determined that glass transitions regions for all tested coatings are located above +50°C. It has been shown that the modification of polymeric matrices with silicon-organic oligomers causes decrease of glass transition temperatures to some extent. Some operational characteristics (isothermal aging, weatherability, photochemical stability, water absorption ability) of elaborated hybrid coatings have been studied.