

ANTIMICROBAL PROPERTIES OF POLYMER NON ORGANIC COMPOSITES ON THE BASIS OF POLYVINYL ALCOHOL

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Key words: PVA, aluminium oxide, iodine, silver iodide, complex, gel, nanoparticle, bactericidal properties

*Polymer-non organic composites are obtained by the method of sol – gel technology on the basis of polyvinyl alcohol and aluminum oxide containing molecular complexes PVA-iodine-boric acid in gel form converted to nonorganic carriers. It is shown that the input of polymeric matrix of nanoparticles in the silver iodide allows to get composite materials having antibacterial activity. The mechanism of nucleation of nanoparticles in the silver iodide mass and their average measurements are determined by the method of lightening. The study of antibacterial activity of polymer-non organic composites obtained containing nanoparticles AgI on tests *Vibrio cholerae* non 01/0139 (N591) and *Bacillus anthracodes* showed their high efficiency. It is proved that the obtained composites have prolonged bactericidal action.*

Introduction

It is obvious that iodine generates molecular complexes with polyvinyl alcohol (PVA) having antiseptic, antimicrobial and fungicidal properties [1]. "Iodinol" as a drug is produced by a pharmaceutical industry representing itself water solution of iodine, iodide calcium and PVA. Recently great interest is shown to the obtaining of advanced gel and solid phase PVA iodine which have not only antibacterial properties but can also function the deposition of molecular iodine [2].

The application of water solvent polymers as matrixes for therapeutic agents led to macromolecular forms of the medicinal preparations having significant advantages over traditional low molecular forms [3]. Thanks to the hydroxyl group, the PVA is adsorbed onto the hydrophilic material and is easily mixed with various fillers [4]. The works on obtaining and studying the composites of PVA with nanomorph levels are of great interest with the purpose to create materials with exploitative properties [5].

On the another hand, while producing new antibacterial preparations the question of the antimicrobial activity of the ions and the metallic silver is continously rising [6-8].

Under the illustration of above mentioned the obtaining of composite materials is represented as interesting which itself is molecular complexes of iodine with PVA in a solid gel form applied on the non organic carrier and the study of the influence of various factors on antimicrobial characteristics of composite.

The aim of the work is to obtain complex PVA iodine acid in solid form applied on the aluminium oxide (Al_2O_3) to determine its antibacterial properties and to study the influence of silver ions on the antimicrobial properties of obtained polymer non organic composites (PNOC).

Conflict setting

The aim of this work is to obtain complexes of boric-iodine acid in the form of gel with PVA applied on aluminium oxide (Al_2O_3) and to determine their antibacterial properties. The process of adsorption of PVA on the surface of aluminium oxide is studied. The chance of using the method of light scattering for determining the sizes of nano particles of silver iodide is shown here. The influence

of nano particles of silver iodide on the antimicrobial properties of obtained polymer-non organic composites is also studied (PPC).

Research results

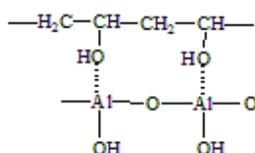
Experimental part. We used the following in our work: aluminium oxide for chromatography “Ch” (TU 6-09-3916-75), 0,1 H iodine solution, 0.01 H solt acid, iodide calcium, boric acid, tetaboronic acid sodium and silver nitrate: all the reactivs of the group “KhCh” and Japanese PVA containing acetate groups $\sim 0.9\%$. The molecular properties of the PVA were determined after reacting (acetylenethane 99.98%) on UV ultrasonic CTM 3180 (Hungary) at 45000 r/pm and with registrations of sedimentation tape with the optical system Philipota-Swenson. The calculation of sediograph was done by the method of fixing ordinates. It is determined that PVA has $MW = 109000$ and molecular mass distribution of $Mw/Mn = 2.1$. The initial oxide of aluminum is subjected to triple processing by sodium solid form at 1:10 ratio at 70°C . After it the multi-stage oxidation of aluminum oxide was done by distilled water to the full removal of ion chlorine. The freshly diluted PVA solutions dissolved in 1% concentration were used in the study. Polymer - non organic composites were obtained following a three-stage process: a) adsorption of PVA to the surface of Al_2O_3 by mixing wet alluminium oxide at $40\text{-}45^{\circ}\text{C}$, b) the introduction of a water solvent with iodide calcium at the temperature of 30°C , c) introduction of the mixed water solvent of boric acid and sodium tetaborate into the reaction system.

When receiving the complexes containing silver iodide, the calculated amount of water solvent of silver nitrate was introduced to the solvent on its initial phase. For determination the average sizes of nanoparticles of AgI model sols were created, iodide calcium was added to the PVA and AgNO_3 by mixing them and the concentrations of components corresponded the concentrations of technological processes of obtaining PCC. The average size of nanoparticles of AgI was determined by spectral turbidimetric method [9] thus removing the dependence of optical density of ash from the length of the wave on photometer KФK-3 in the range of $\lambda = 350\text{-}650$ nm at the temperature of $20\text{-}22^{\circ}\text{C}$.

The study of bactericidal properties was followed by the following methodology. Each piece of composites for 1 g was collected in each of the three tubes with 10, 20 and 30 ml of distilled water (corresponding to the composite: water = 1: 10; 1:20, 1:30). The tubes where PPC relation comprises 1:10 and 1:20 lasted for 24 hours and the tubes with 1:30 lasted for 24, 36 and 48 hours per periodic mixing in the protected from sunlight area for the diffusion of the active components in the water phase. The definition of bactericidal properties of composites were proven by 4 hour and daily crops *Vibrio cholerae non 01/0139 (N591)* grown on acetic agar (pH 7,8, series 135) and daily sort *Bacillus anthracodes* grown on Hothinger agar (pH 7, 3 series 6) at incubation temperatures of 22°C and 37°C . The ingredients were tested by defining a method for the zones of inhibition of bacterial growth round the holes with a water - borne fluid tested in an amount of 50 mkl. Zone inhibition was detected after 24 h. At the same time the cultivation was done by controls of the crops and studied samples.

Results and discussions. The choice of Al_2O_3 is determined by that it is one of the polar adsorbents the features of which can be varied in wide boundaries of regulation of acid based characteristics of the surface as a means of obtaining and also as a means of chemical prossessing [10]. In its turn PVA forms complexes and chemical connections with ions of the table of chemical elements [11].

Adsorption of PVA on the surface of Al_2O_3 in the first phase happens in two stages. In the first stage the irreversable process of chemisorbtion with the formation of interpolymer complex of suggested structure [12]:

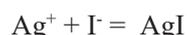


The irreversibility of adsorption was confirmed by studying the desorption of adsorbed PVA on the formation of iodine complex with atoms of PVA which are connected with the surface of aluminium oxide. In the second stage the process of adsorption of polymolecular polymer goes on the formation of the chemisorption layer of PVA.

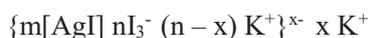
After homogenization, in the second stage of introduction of iodine water solvent with KI, mixed solvent of H_3BO_3 and $Na_2B_4O_7$ is introduced into reaction mixture. Therefore the formation of complex PVA happens $I_2 - H_3BO_3$ accompanied by gelling of the system which turns into solid gel (**Sample №1**).

When obtaining the sample of composite containing the silver ions, in the process of adsorption of Ag^+ the following reaction happens with polymolecular adsorption layer of PVA. Indeed, possibly, the orientation of silver ions occurs related with negatively charged centre of formation of PVA with aluminium oxide. It is also obvious that in the regime of temperature of adsorption process ($40-45^\circ C$) the partial regeneration of silver ions happens by aldehydes and at least hydro acid groups of PVA [13]. After the introduction of iodine solution into the reaction system with KI the formation of nano particles of silver iodide occurs in polymer matrix.

The process of formation of nano particles has kinetic character and the scheme of the process may be presented in the following way. Silver atoms form clusters formed in the process of partial regeneration of ions Ag^+ . It is more possible that in the presence of additional silver ions the clusters of Ag_8^{2+} composite comprises tens of minutes during the existence of clusters [14]. When introducing the water solvent of iodine and iodide calcium clusters of silver reacting the ions of I_3^- into the reaction system they turn into clusters AgI which are the seedlings of nano particles of silver iodide. Simultaneously the nucleation of AgI flows along the homogenous mechanism according to the following reaction:



Consequently, precursors of nano particles of AgI are the clusters of silver Ag_8^{2+} and also the silver nitrate. The average sizes of particles are calculated by the method of spectrum of turbidity and the formula of Reley formed in the sample solvents of PVA. It is defined that the diameter of particles is located in the interval of 55-70 nano meters. Nano particle AgI can be presented by the following formula:



where $m \gg n$, $n > x$.

Taking into account the size effects of phase and structural transformations of polymorpheme connections into nano systems, it may be supposed that silver iodide has cubic structure [15]. In case of affecting on the given system of boric ions solid gel is formed representing itself a composite from nano particle of iodide calcium and molecular complex PVA flowing on the surface of aluminium oxide (**Sample №2**).

The results of studying the antibacterial characteristics of studied samples PCC are shown in the Tables 1 and 2. It is obvious that the Sample №1 representing itself gel substance of the preparation "iodine" does not affect the growth of experimented sorts.

On the contrary, Sample №2 which contains nano particles of silver iodide showed high bactericidal activity related to both *Vibrio cholerae non 01/0139(N591)* and *Bacillus anthracodes*. High bactericidal activity of Sample №2 may be conditioned by the presence of silver ions Ag^+ in

water phase formed in the case of dissociation of silver iodide immobilized in polymer matrix and also, which is more possible, by the impact of synergy mechanism of silver ion and triiodide ions on the experimented crops. The choice of silver iodide was defined by two reasons: firstly, by the presence of iodide –triiodide in the system, and secondly, by very low solution of silver iodide in the water ($IP_{AgI} = 8.3 \cdot 10^{-17}$). The data presented in Table 1 and 2 show the following:

Table 1

Impact of the samples on the growth of the 4 and 24 hour crops *Vibrio cholerae* non 01/0139 N159 in exposition 22°C and 37°C

“-“ - the crop is not under pressure, “+++” - the crop is under pressure completely, the number is in mm-the dimension of the pressure zone, “*”- aging 36 hours, “**”- aging 48 hours.

| Number of the sample and degree of cultivation | Vibrio cholerae non 01/0139 N159 (10^3 q.t.a./ml) | | | | |
|--|--|----------|--------------|-----------|-----------------------------|
| | 4 hour crop | | 24 hour crop | | Control over the crop |
| | 22 °C | 37°C | 22°C | 37°C | 37°C |
| №1(1:10) | - | - | - | - | Complete growth of the crop |
| №1(1:20) | - | - | - | - | |
| №1(1:30) | - | - | - | - | |
| Control of the sample | Without external microflora | | | | |
| №2(1:10) | 10mm/+++ | 10mm/+++ | 10mm/+++ | 10mm/+++ | |
| №2(1:20) | 8mm/++ | 8 mm/++ | 8 mm/++ | 8 mm/++ | |
| №2(1:30) | 5 mm/+ | 5 mm/+ | 5 mm/+ | 5 mm/+ | |
| №2(1:30)* | 7mm/+ | 7mm/+ | 7mm/+ | 7mm/+ | |
| №2(1:30)** | 9.5mm/+++ | 10mm/+++ | 10mm/+++ | 9.5mm/+++ | |
| Control of the sample | Without external microflora | | | | |

By the increase of the water content in the ratio of PCC the following happens: decreases the bactericidal activity of the composite. The decrease in the bactericidal effect of Sample №2 on the tested crops with an increase in the amount of water at a ratio of PCC: water = 1:30 during the aging of the system for 24 hours is determined by a decrease in the concentration of active components in the water phase. Obviously, it is the process of diffusion of Ag + and I₃⁻ ions from the polymer matrix that is the limiting stage of achieving an equilibrium concentration of ions in the water phase as the data in Tables 1 and 2 clearly indicate.

There is an increase in bactericidal activity up to the leveling effect of the difference in the amount of water in the ratio of PCC. In the resulting composite silver iodide is localized in a crosslinked polymer matrix of PVA in the form of nanoparticles having sufficiently large molecular weight. The limited swelling of crosslinked PVA in water leads to a significant decrease in the local concentration of silver ions due to a decrease in the actual amount of water in the polymer matrix.

Table 2

Impact of the samples on the growth of 24 hour crops *Bacillus anthracoides* in exposition 22°C and 37°C

“-“ – crop is not under pressure, “+++” - crop is under pressure completely, number is in mm - the dimension of the pressure zone, “*”- aging 36 hours, “**”- aging 48 hours.

| Number of sample and degree of cultivation | Bacillus anthracoides (10 ³ q.t.a./ml) | | |
|--|---|-----------|-------------------------|
| | Zone of inhibition, mm | | Control of sample |
| | 22°C | 37°C | 37°C |
| №1(1:10) | - | - | Complete growth of crop |
| №1(1:20) | - | - | |
| №1(1:30) | - | - | |
| Control of sample | Without external microflora | | |
| №2(1:10) | 10 mm/+++ | 10 mm/+++ | |
| №2(1:20) | 9 mm/++ | 9 mm/++ | |
| №2(1:30) | 8 mm/+ | 8 mm/+ | |
| №2(1:30)* | 9mm/++ | 9mm/++ | |
| №2(1:30)** | 10mm/+++ | 10 mm/+++ | |
| Control of sample | Without external microflora | | |

By varying the degree of crosslinking of the PVA, it is possible to regulate the degree of swelling of the polymer matrix and, accordingly, the amount of water contained in it. The water solution in the polymer matrix has high viscosity which depends on the molecular weight and the degree of crosslinking of the original PVA. High viscosity of the solution in the polymer matrix will lead to a decrease in the diffusion rate of silver ions and triiodide ions from the matrix into the water phase and lead to a prolonged delivery of the active component to the infected zone.

Conclusion

In this work the possibility of obtaining a composite material representing the molecular complex of iodine with PVA (an analog of the pharmaceutical preparation “Iodinol”) applied on a non organic carrier has been shown for the first time. It was determined that the introduction of silver iodide nanoparticles into the polymer matrix leads to a significant increase in the bactericidal activity of PCC. It was shown that intermolecular crosslinking of PVA chains with boric ions allows to control the diffusion rate of the active components in the water phase. The prolonged nature of the effect of PCC on pathogenic crops opens up a wide practical spectrum of using the obtained composites for both therapeutic and disinfecting purposes.

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ՈՒՏԴ - 678:546.55:544.77

**ՊՈԼԻՎԻՆԻԼ ՍՊԻՐՏԻ ՀԻՄՔԻ ՎՐԱ ՊՈԼԻՄԵՐ – ԱՆՕՐԳԱՆԱԿԱՆ
ԿՈՍՊՈԶԻՑԻԱՆԵՐԻ ՀԱԿԱՍԻԿՐՈՒՄՅԻՆ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ**

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Զուլ-գելային տեխնոլոգիաների մեթոդով ստացված են պոլիմեր-անօրգանական կոմպոզիտներ, պոլիվինիլ սպիրտի և ալյումինի օքսիդի հիմքի վրա՝ կազմված ՊՎՍ-յոդ – բորաթթու մոլեկուլային կոմպլեքսներից գելային տեսքով, որոնք տեղադրված են անօրգանական կրիչի վրա: Ցույց է տրված, որ պոլիմերային մատրիցայի մեջ մտցված արծաթի յոդիդի նանոմասնիկները թույլ են տալիս ստանալ կոմպոզիցիոն նյութեր, որոնք օժտված են հակամիկրոբային ակտիվությամբ: Վերանայված է արծաթի յոդիդի նանոմասնիկների նուկլեացիայի մեխանիզմը և լուսացրման եղանակով որոշված են նրանց միջին չափսերը: Ստացված պոլիմեր-անօրգանական կոմպոզիտների հակամիկրոբային ակտիվության ուսումնասիրությունը, որոնք պարունակում են արծաթի յոդիդի նանոմասնիկներ *Vibrio cholerae non 01/0139(N591)* և *Bacillus anthracodes* թեստ կուլտուրաների վրա, ցույց են տվել նրանց բարձր

Էֆեկտիվությունը: Ցույց է տրված , որ ստացված կոմպոզիտները օժտված են երկարատև հակամիկրոբային հատկությամբ:

Բանալի բաներ. ՊՎՍ, ալյումինի օքսիդ, յոդ, արծաթի յոդիդ, գել, նանոմասնիկներ, բակտերիասպան հատկություն:

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АНТИМИКРОБНЫЕ СВОЙСТВА ПОЛИМЕР-НЕОРГАНИЧЕСКИХ КОМПОЗИЦИЙ НА ОСНОВЕ ПОЛИВИНИЛОВОГО СПИРТА

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Մեթոդով շոլ-ձել-տեխնոլոգիա թուլաշեն քոլիմեր-նեօրգանիշեսքիե կոմքոզիտի յոն յոլիվինիլօվօգո սքիրտա և օքսիդա ալյումինիա, սօսթաշիե իշ մօլեկուլարնիե կոմքոզիտի ՔՎՍ-յօդ-քոռնա կիսլօտա յո ձելօվօյ ֆօրմե, նանեսեննի յո նեօրգանիշեսքի յոսիթել. Քօաշանօ, շո յոլեձենիե յո քոլիմերնա յո մաթրիշա նանօշաշիտի յօդիդա սերեբրա թօլաշալթ թուլաշեն կոմքոզիտիոննե մաթերիալա, օլաձաաշիե անտիբաքտերիալնօյ աքտիվնօշա. Քասմօթրեն մեքանիշմ նուկլեաշիոն նանօշաշիտի յօդիդա սերեբրա և մեթոդով սվետօրասեյանիա օրեձելեն իք սրեձնե հաշմեր. Իսսլեձօվանիե անտիբաքտերիալնօյ աքտիվնօշի թուլաշեննի քոլիմեր-նեօրգանիշեսքիե կոմքոզիտօվ, սօձերձաշիե նանօշաշիտի AgI յո տես կուլթուրաք Վիբրիօ շոլերաե յոն 01/0139(N591) և Յաքիլլուս անթրաքօձես թօաշալթ իք յոլաշօքոյա էփֆեքտիվնօշ. Քօաշանօ, շո թուլաշեննե կոմքոզիտի օլաձաաշի թրօլոնգիրօվաննիմ քաքտերիշիձնիմ ձելաշիեմ.

Կլաշեվե սլօվա: ՔՎՍ, օքսիդ ալյումինիա, յօձ, յօդիդ սերեբրա, կոմքոզիտ, ձել, նանօշաշիտ, քաքտերիշիձնե սվօշաշիա.

Ներկալալաղվել է՝ 18.01.2019թ.

Գրալիտաձան է ուղարկվել՝ 24.01.2019թ.

Երաշխալաձորվել է տպագրության՝ 26.04.2019թ.