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Influence of modification of surgical sutures with film coatings based on chitosan, polyvinyl alcohol and Na-carboxymethylcellulose dialdehyde on their capillary and physico-mechanical properties

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The study of capillarity for polycaproamide braided sutures of metric sizes No. 4 and No. 5 before and after modification by coating based on chitosan, polyvinyl alcohol and Na-carboxymethylcellulose dialdehyde was carried out. It was found that the capillarity of the original braided polycaproamide sutures increases with increasing their metric size. The capillarity of the polycaproamide sutures decreases by 6–10 times after applying the modifying coating. The maximum decrease in the capillarity is achieved by additional modification of the coating with a solution of sodium dodecyl sulfate, which leads to a maximum increase in the contact angle. The influence of the coating on the physical and mechanical properties of the original and modified polycaproamide sutures has been established. It is shown that the applied coating leads to a decrease in the tensile strength and an increase in the relative elongation at break of polycaproamide sutures. The obtained values for sutures of metric size No. 5 are within the allowable requirements of the USP. The results of the study can be used to create surgical suture material with improved performance characteristics and a lower probability of developing implant-associated complications when used in the field of reconstructive plastic and abdominal surgery.

Keywords: surgical suture, capillarity, polycaproamide, chitosan, dialdehyde Na-carboxymethylcellulose.

Вплив модифікації хірургічних ниток плівковими покриттями на основі хітозану, полівінилового спирту та діальдегіду Na-карбоксиметилцелюлози на їх капілярні та фізико-механічні властивості. *С.В.Кривець, Г.І.Ковтун, А.Г.Мисюра*

Досліджено капілярність полікапроамідних плетених ниток метричних розмірів №4 та №5 до та після модифікації покриттям на основі хітозану, полівінилового спирту та діальдегіду Na-карбоксиметилцелюлози. Виявлено, що капілярність вихідних плетених капронових ниток зростає зі збільшенням їх метричного розміру. Після нанесення модифікуючого покриття капілярність капронових ниток знижується у 6–10 разів. Максимальне зниження капілярності досягається додатковою модифікацією покриття за допомогою розчину додецилсульфату натрію, яке призводить до максимального збільшення крайового кута змочування. Встановлено вплив покриття на фізико-механічні властивості вихідних і модифікованих полікапроамідних шовних ниток. Показано, що створене покриття призводить до зменшення границі міцності на розрив та збільшення відносного видовження при розриві полікапроамідних шовних ниток. Отримані значення для ниток метричного розміру №5 знаходяться в межах допустимих вимогами USP. Результати дослідження можуть бути використані для створення хірургічного шовного матеріалу з покращеними експлуатаційними характеристиками та меншою вірогідністю розвитку імплантат-асоційованих ускладнень при його застосуванні в галузі реконструктивної пластичної та абдомінальної хірургії.

Исследована капиллярность поликапроамидных плетеных нитей метрических размеров №4 и №5 до и после модификации покрытием на основе хитозана, поливинилового спирта и диальдегида Na-карбоксиметилцеллюлозы. Выявлено, что капиллярность исходных плетеных поликапроамидных нитей растет по мере увеличения их метрического размера. После нанесения модифицирующего покрытия капиллярность поликапроамидных нитей снижается в 6–10 раз. Максимальное снижение капиллярности достигается дополнительной модификацией покрытия с помощью раствора додецилсульфата натрия, которая приводит к максимальному увеличению краевого угла смачивания. Установлено влияние покрытия на физико-механические свойства исходных и модифицированных поликапроамидных шовных нитей. Показано, что созданное покрытие приводит к уменьшению предела прочности на разрыв и увеличению относительного удлинения при разрыве поликапроамидных шовных нитей. Полученные значения для ниток метрического размера №5 находятся в пределах, допустимых требованиями USP. Результаты исследования могут быть использованы для создания хирургического шовного материала с улучшенными эксплуатационными характеристиками и меньшей вероятностью развития имплантат-ассоциированных осложнений при его применении в области реконструктивной пластической и абдоминальной хирургии.

1. Introduction

Due to their structure, polyfilament surgical sutures have good manipulative properties: they are soft and flexible, firmly held in the hand, form a reliable knot [1]. However, due to the bonding of fibers by braiding or twisting, the surface of the multifilament suture is uneven, resulting in soft tissue damage [2]. In addition, due to the multi-fiber structure, polyfilament sutures have high capillarity [3–5], that contributes to the spread of fluid and microorganisms along the suture, the biological leakage of the suture and the development of infection.

According to some authors, for most operations, complex suture with coating are most acceptable, combining the positive properties of mono- and polyfilament sutures [3–5]. The polymer coating smoothes the surface of the suture material and fills the interfiber space, reducing capillarity and "sawing" effect to a minimum [6]. At the same time the suture with a coating has good manipulative properties which are characteristic for typical polyfilament materials [7–9].

The coating material for surgical sutures must be biocompatible and non-reactogenic. One of its most promising characteristics is the polysaccharide chitosan, the macromolecules of which consist of randomly linked β-(1 → 4)-D-glucosamine and N-acetyl-D-glucosamine units. It is widely used in biomedical engineering due to its unique characteristics such as apyrogenicity, high biocompatibility, ability to hydrolytic biodegradation, bactericidal action, anti-inflammatory and hemostatic effects [10, 11]. In this regard, chitosan and its derivatives are widely used in biomedical practice for the manufacture of continuous and structured gels, sorbents for targeted and prolonged drug transport. Gel and film materials based on native and modified chitosan have proven themselves as implants for bone fusion, artificial skin substitutes for burns, hemostatic agents in surgery and traumatology [12–16].

To improve the physical and mechanical properties of chitosan coatings, other polymers are introduced into their composition. For example, polyvinyl alcohol (PVA), due to its biocompatibility, is used to produce hydrogels for biomedical use, including in combination with chitosan.

Chitosan dissolved in an acidic medium is able to form a three-dimensional network of gel upon addition of chemical cross-reacting agents due to the binding of amino and hydroxyl groups. Phthalic and amber dianhydrides, diepoxides, crown ethers, divinyl sulfone, aldehydes of various structures (glutaraldehyde, genipin, formaldehyde, acetaldehyde, glyoxal, oligoethylene glycol) are used as cross-linking agents. Glutaric aldehyde reacts most easily with amino groups, but the presence of crotonic condensation products of glutaric aldehyde in crosslinked chitosan samples [17] limits the use of the chitosan-aliphatic dialdehyde system for biomedical purposes. Therefore, it is very important to find new crosslinking reagents that can, like glutaraldehyde, react effectively with chitosan and polyvinyl alcohol to form hydrogels, but not to form oligomeric products.

In this case, the use of dialdehydes obtained by periodic oxidation of monosaccharides, polysaccharides, glycosaminoglycans, etc. is very promising. For example, car-

boxymethylcellulose dialdehyde has shown good results in crosslinking of hydrogels of gelatin [18], polyvinyl alcohol [19], carboxymethylchitosan [20], and chitosan [21]. The obtained gels had better thermal stability, swelling ability and cytocompatibility in comparison with gels crosslinked with glutaraldehyde.

Modern research has shown that the coating of surgical sutures can affect their mechanical properties, due to the nature of both the sutures and the coating used. Thus, the coating based on graphene oxide with dopamine hydrochloride contributed to a decrease in the strength and elongation at break of polyfilament sutures based on polyglycolic acid [8]. In [22] it was shown that the composition of the shell and the molecular weight of the polymers used also affect the mechanical properties. The authors found that the coating based on polyhydroxybutyrate as a whole contributes to an increase in strength and a decrease in elongation at break of sutures of different nature (kapron, lavsan). Thus, determining the effect of the coating on the mechanical properties of the sutures is important to establish compliance with the requirements of the USP (United States Pharmacopeia) for surgical sutures.

The aim of this study is to determine the effect of a film coating based on chitosan, polyvinyl alcohol and Na-carboxymethylcellulose dialdehyde on the physical, mechanical and capillary properties of polycaproamide sutures.

2. Experimental

We used polycaproamide sutures of metric sizes (MS) No.4 and No.5, polyvinyl alcohol (PVA) with a molecular weight of 120 kDa, chitosan with a molecular weight of 75 kDa and a degree of deacylation of 70 %, dextran with a molecular weight of 14 kDa, Na-carboxymethylcellulose (Na-CMC) 20 kDa, glycerin, sodium dodecyl sulfate (SDS).

To obtain a 2 % solution of chitosan in 2 % acetic acid, it was mixed to a homogeneous state on a magnetic stirrer for 2–3 h at a temperature of 30–37°C. The pH of the solution was maintained at 3.9. Distilled glycerin was also added to the chitosan solutions in an amount of 2 % by volume of the working solution to ensure the elasticity of the coating. A 6.355 % solution of polyvinyl alcohol and a 0.5 % solution of dextran sulfate were prepared in 2 % acetic acid.

To obtain Na-CMC dialdehyde, periodic oxidation in aqueous solution of Na-CMC was performed. The degree of oxidation in the reaction product was determined by the iodometric method by ion IO_4^- consumption and using a spectrophotometer by changing the intensity of the absorption band at a wavelength of 222 nm. After that, a solution of dialdehyde Na-CMC 1M with the addition of acetic acid was prepared until reaching a pH level of 8.76±0.02.

To apply the modifying coating, the initial suture was successively passed through three baths with solutions at a speed of 1.8 m/min, taken out through a calibrated hole to remove excess solution and dried in air flow with a temperature of 120°C. The first bath was filled with 3 % sodium periodate solution, which was used to remove lubricants and activate the surface of braided polycaproamide sutures. The second bath was filled with a mixture of solutions of chitosan, PVA, dextran and distilled glycerin in 2 % acetic acid; the pH of the solution was maintained at 4.0. The third bath was filled with a mixture of solutions of chitosan, PVA, dialdehyde Na-CMC and glycerin in 2 % acetic acid. A fourth bath with 0.3 % sodium dodecyl sulfate solution in distilled water was used in a number of experiments.

The amount of the coating was determined by weighing the suture before and after modification. The thickness of the obtained coatings was not more than 35 μm. Capillarity of the original and modified sutures was determined according to ISO 811-81. The end of the vertically suspended suture was immersed in a 10^{-3} M aqueous solution of Oxazine; then the height of rise of the colored liquid h_t at time t was measured for several hours of exposure and the obtained data were plotted. Since the measurement took a long time, the suture was placed inside the capillary to reduce the evaporation of the solution ascending along the suture.

Experimental determination of the maximum height of liquid rise on the vertical sample may be complicated by swelling of the suture fibers [23]. To eliminate the error that occurs during prolonged contact of water with the fibers, a method of calculating of the maximum height of liquid on the suture sample at the initial interval of the kinetic curve was proposed in [23, 24]. According to the authors, the method of determining these parameters is quite accu-

rate and the calculation error does not exceed 0.5 %.

The parameters of the capillary structure of the initial and modified sutures were calculated according to the method described in [23]. The parameters were the maximum height of the liquid rise h_{max}, the smallest radius of capillaries r_{min} and the contact angle Θ.

Equation (1) [23] was used to process the kinetic curves.

$$h_t = \frac{h_{\max} t}{(t + t_0)}, \quad (1)$$

where t is the rise time of the dye solution in the suture sample; t_0 is the time of filling of half of the maximum height of liquid rise in the suture sample; h_t is the height the rise of the dye solution in the suture sample at time t; h_{max} is the maximum capillary filling height in the suture material, corresponding to the height of the liquid meniscus rise in the capillary in equilibrium. Equation (1) can be written in the following linear form (2):

$$\frac{t}{h_t} = \frac{t_0}{h_{\max}} + \frac{t}{h_{\max}}. \quad (2)$$

Further, the graphs of the dependence of t/h_t on time t were plotted. The obtained points were used to construct a straight line using the least squares method. The parameters of the found line were used to determine the value of the rise limit of the dye solution in the suture sample h_{max} and the time to fill half the height of the maximum liquid rise in the suture sample t_0. If the shape of the capillaries is cylindrical, the Washburn capillary flow kinetic equation has the following form (3) [25]:

$$h_{\max} \ln \frac{h_{\max}}{h_{\max} - h_t} - h_t = \frac{r^2 \rho g}{8\eta} t, \quad (3)$$

where r is the capillary radius; ρ is the liquid density (for water at 20°C ρ = 1000 kg/m^3); η is the liquid viscosity (for water at 20°C η = 10 Pa·s); g is the gravitational acceleration 9.8 m/s^2.

The smallest capillary size r_{min} was calculated based on the assumption that the error of the experiment is 0.5 %. In this regard, according to the equation (2) the time $t_{0.995}$ required to raise the dye solution to a height of $h_t = 0.995 h_{max}$ was calculated. Then the smallest capillary radius r_{min} was found using the Washburn equation (3), taking $h_t = 0.995 h_{max}$.

According to the found values of h_{max} and r_{min}, the cosine of the contact angle Θ was calculated according to Jurin's equation (4) [25]:

$$\cos\Theta = \frac{h_{\max} \rho g r_{\min}}{2\sigma}, \quad (4)$$

where σ is the surface tension of wetting liquid (for water at 20°C σ = 72.75 mJ/m^2).

The surface tension values of 10^{-3} M aqueous oxazine solution were taken equal to the surface tension of water in equation (4), because the experimental determination of σ by capillary lifting revealed no significant difference between the surface tension of water and the oxazine solution.

Tests of the sutures for uniaxial stretching were performed at a temperature of 20°C and a relative humidity of 75 % according to the Russian National Standard 31620-2012. The rate of deformation in all tests was the same $8.3 \cdot 10^{-4}$ s^{-1}. Suture samples for testing were formed with two loops at the ends with a working length (inter-nodal distance) of 100 mm. The tensile strength and elongation at break for the original and coated suture samples were determined.

3. Results and discussion

As a result of a series of experiments, the kinetic curves of the rise of the Oxazin dye solution were obtained on vertically suspended samples of suture material of metric sizes No. 4 and No. 5 after penetration through the end of the suture material (Fig. 1).

The rise rate was maximum in the first 5 min. Then a gradual decrease in the rise rate of the dye solution was observed, and after 30 min the curves tended to reach the plateau. In [23], to eliminate the error caused by prolonged contact of water with fabric fibers due to their swelling, a method was proposed for calculating the maximum liquid height on a fabric sample at the initial interval of the kinetic curve. Accordingly, the height of the dye solution h_t for time t = 30 min was taken as an indicator suitable for comparing the capillarity of different suture samples. The obtained curves were used to calculate the parameters of the capillary structure of braided polycaproamide sutures (Table).

It was found that the original sutures with a higher metric size (MS) exhibit a higher dye

Table. Parameters of the capillary structure of the original and modified polycaproamide sutures

	h_t, mm	r_{min}, μm	cos Θ	Θ, °	h_{max}, mm
Braided polycaproamide suture of MS No. 4					
Original	95	1.88	0.0174	89	136.7
Modified with a polymer coating	43	1.79	0.0058	89.67	48
Modified with a polymer coating and treated with SDS	8	0.36	0.0004	89.98	16.6
Braided polycaproamide suture of MS No. 5					
Original	101	1.79	0.0178	88.98	148
Modified with a polymer coating	38	1.50	0.0043	89.75	42.4
Modified with a polymer coating and treated with SDS	10	0.41	0.0005	89.97	19.7

solution height h_t. This is due to the different radii of capillaries in the sutures of different MS. The contact angle Θ of the sutures of both MSs is almost the same; and the minimum capillary radius r_{min} in the sutures of MS No. 5 is almost 0.1 μm smaller than in the sutures of MS No. 4.

The study of the effect of the modifying coating on the capillarity of the sutures showed that after coating, the capillarity of the polycaproamide sutures significantly decreases. For sutures of MS No. 4, the maximum dye solution height h_{max} decreased by 65 % compared to the original sutures, and for sutures of MS No. 5 it decreased by 71 %.

It was found that after coating the surface of polycaproamide sutures, the smallest calculated capillary radius r_{min} decreases slightly, and the contact angle Θ increases by 0.7–0.8°. This allows us to conclude that the main effect on reducing the capillarity of the sutures has a decrease in their wetting, i.e. the surface of the suture becomes more hydrophobic.

A decrease in the calculated radius of the capillaries shows that the application of the polymer coating leads to the filling of large capillaries, reducing the total number of capillaries, thereby blocking the path of liquid propagation along the suture.

To test the effect of hydrophobicity of the coating on the capillarity of the suture, an attempt to increase the hydrophobicity of the created coating by modification with sodium dodecylsulfate was made. SDS is an anionic surfactant capable of forming ionic bonds with protonated chitosan amino groups. As a result of such treatment, a water-insoluble layer of a surfactant-polyelectrolyte complex is formed on the surface of the chitosan film [26–28]. In order to confirm the modification of the surface of the chitosan film by SDS, we have previously created films based on chitosan acetate and a mixture of chitosan acetate/PVA, which were kept in a solution of SDS, and then dried. The modified films did not dissolve when exposed to saline during the day and swelled to 672 % (chitosan) and 526 % (chitosan/PVA), while the unmodified films were completely dissolved. Additional treatment of polycaproamide sutures with a polymer coating in a solution of SDS leads to a decrease in capillarity (Fig. 1).

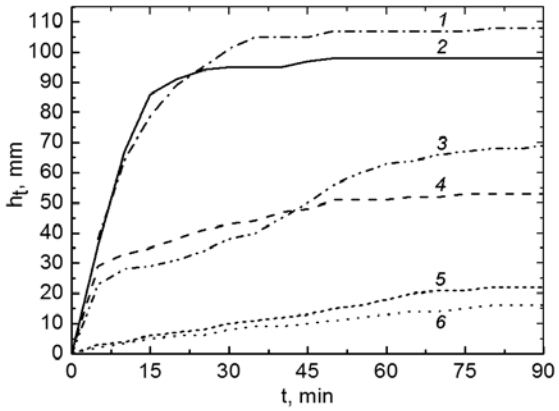

Fig. 1. Kinetic curves of the rise height of Oxazine solution on surgical sutures: *1* — original suture MS No.5, *2* — original suture MS No. 4, *3* — modified suture MS No. 5, *4* — modified suture MS No. 4, *5* — modified and treated with SDS suture MS No.*5*, *6* — modified and treated with SDS suture MS No.*4*.

Calculations showed that the contact angle of the capillary walls increases to 89.98° and the smallest calculated capillary radius decreases. The maximum dye solu-

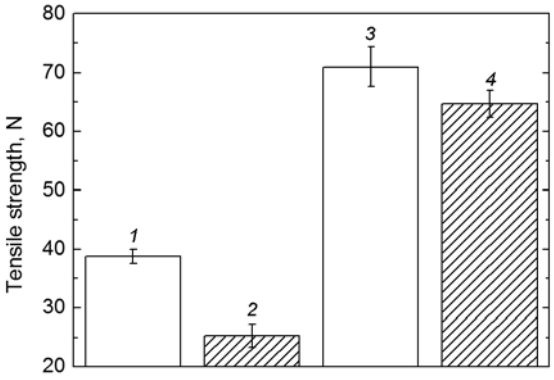

Fig. 2. Tensile strength of original and modified with a polymer coating sutures ($p < 0.05$): *1* — original suture MS No. 4, *2* — modified suture MS No. 4, *3* — original suture MS No. 5, *4* — modified suture MS No. 5.

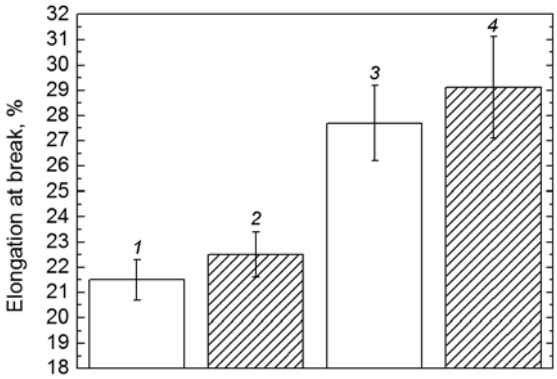

Fig. 3. Relative elongation at break of the original and modified with a polymer coating sutures ($p < 0.05$): *1* — original suture MS No. 4, *2* — modified suture MS No. 4, *3* — original suture MS No. 5, *4* — modified suture MS No. 5.

tion height was 16.6 and 19.7 mm for the sutures of MS No. 4 and No. 5, respectively, which is 87.9 and 86.7 % lower than the dye solution height for the original sutures without coating (Table).

According to the requirements of USP for synthetic surgical sutures of metric size No. 4, the diameter should be from 400 μm to 499 μm, and for metric size No. 5 — from 500 μm to 599 μm. The thicknesses of the applied coatings were not more than 35 μm, which does not exceed the permissible deviation of 99 μm, so the metric sizes of the sutures remained unchanged.

In a series of experiments, the values of the tensile strength (Fig. 2) and the relative elongation at break (Fig. 3) for the original and modified sutures of MS No. 4 and MS No. 5 were determined. The data are presented with a significance level of $p < 0.05$. For both metric sizes, a decrease in the tensile strength and some increase in the relative elongation at break of the modified sutures in comparison with the original were observed. It was found that the tensile strength in the modified sutures of MS No. 4 decreased by 34.8 %, and in the modified sutures of MS No. 5 by 8.9 % compared to the original. The elongation at break increased in the modified sutures of MS No. 4 by 4.7 %, and in the modified sutures of MS No. 5 — by 5.1 % compared to the original. According to the requirements of the USP, the maximum tensile strength in a simple knot for synthetic sterile non-absorbable surgical sutures should be 26.7 N for MS No. 4, and 34.5 N for MS No. 5; for non-sterile sutures, these are 33.4 and 43.1 N, respectively. Experimental studies have shown that after modification, the sutures of MS No. 4 ceased to comply with USP tensile strength requirements, while the sutures of MS No. 5 fully comply with USP tensile strength requirements. Thus, it is necessary to carry out additional studies of the influence of the composition of the coating and the polymer shell in order to increase the tensile strength of sutures with MS No. 4.

4. Conclusions

The capillarity of the original braided polycaproamide sutures increases with increasing their metric size. A study of the effect of a modifying coating based on chitosan, polyvinyl alcohol and Na-carboxymethylcellulose dialdehyde on the capillarity of the sutures showed that the coating reduces the capillarity of polycaproamide sutures by 6–10 times. This is due to the filling of the capillaries located closer to the surface of the sutures and to some increase in the contact angle. The contact angle of the liquid has a greater effect on the capillarity than the radius of the capillaries. It is shown that the applied coating promotes a decrease in the tensile strength and an increase in the relative elongation at break of polycaproamide sutures. The obtained values for sutures of MS No. 5 are within the allowable USP requirements. However, the tensile strength for sutures of MS No. 4 becomes less than the allowable, which indicates the need to vary the composition of the coating and conduct additional research. The results of the study can be used to create surgical suture material with improved performance characteristics and a

lower probability of developing implant-associated complications when used in the field of reconstructive plastic and abdominal surgery.

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