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OPTIMIZATION OF THE OXIDATION REACTION OF VISCOSE USING NITROGEN DIOXIDE

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Abstract

Oxidized cellulose (monocarboxylic cellulose) is a cellulose derivative that has wide practical application in medical practice as a hemostatic coating and bioabsorbable agents. In this work, oxidized cellulose was synthesized by the method of oxidation of viscose (regenerated cellulose) fabric with nitrogen dioxide. For this, the viscose fabric was oxidized with nitrogen dioxide in two ways (pre-moistening with carbon tetrachloride and without wetting). The effect of reaction conditions on the degree of oxidation of the reaction product was studied. Physical and chemical research methods established structural changes in oxidized viscose. Studies have shown that the oxidation rate of products obtained by the CCl_4 pre-moistening method is higher than that of the traditional method.

Keywords: *oxydized viscose, nitrogen dioxide, carboxyl groups, monocarboxycellulose*

Introduction

Stopping bleeding during surgery today is one of the urgent problems of modern medicine. The first step in treating open wounds and injuries is to stop the bleeding quickly. In this case, cellulose derivatives, which are natural polymers, can be used. One of the most used cellulose-based hemostatic drugs is oxidized cellulose (monocarboxycellulose or 6-carboxycellulose). The use of oxidized cellulose as a local hemostatic agent in medicine began in the middle of the 20 th century (Sundaram, S. P., & Keenan, A. S., 2010). Many hemostatic materials are derived from natively oxidized cellulose or oxidized regenerated cellulose (viscose) (Lewis, K.M., Spazierer, D., Urban, M.D., Lin, L., Redl, H., & Goppelt, A., 2013).

Today, hemostatics of various brands are used based on oxidized cellulose (for example, Gelita-Cel, Traumastem, Okcel) which are widely used in medicine, in particular, cardiovascular surgery, neurosurgery, traumatology, general surgery, oncology, ENT surgery, etc. to stop capillary, venous, and small arterial bleeding (Zhong, Y., Hu, H., Min, N., Wei, Y., Li, X., & Li, X., 2021).

Hemostatic agents based on oxidized cellulose contain 16–24% carboxyl groups. The content of bound nitrogen does not exceed

0.5 wt.%, which is a necessary condition for the use of oxidized cellulose in medicine (Mognonov, D.M., Morozov, S.V., Ayurova, O.Z., Chernyak, E.I., Rodionov, V.I., Grigor'eva, M.N., et al., 2019). An important characteristic of oxidized cellulose is its resorption in the tissues of a living organism. The rate and duration of resorption of oxidized cellulose in the body depend on its quantity and place of application and is 30–40 days for hemostatic gauze, 20 days for hemostatic viscose, and 7–14 days for materials based on oxidized viscose. Currently, oxidized cellulose can be obtained in various forms: knitted fabric, powder, non-woven fiber, etc. (Kumar, V., 2003).

Moreover, oxidized cellulose is approved for use in medicine in many countries of the world because of its pronounced hemostatic effect, as well as wound healing, immunostimulating, antibacterial, and antiviral effects, and is completely absorbed in the tissues of a living organism. Oxidized cellulose is non-toxic, does not cause noticeable inflammatory and allergic reactions in body tissues, and has a stimulating effect on the proliferative function of connective tissue (Bajerova, M., Krejcova, K., Rabiskova, M., Gajdziok, J., & Masteikova, R., 2009). Most often, it is used in the form of tissue, making it possible to model it in size and place it on a wound of any configuration.

Oxidized cellulose also has an antimicrobial effect against a wide range of pathogenic microorganisms due to its acidic properties (pH = 2.0–4.0). The antimicrobial properties of oxidized regenerated cellulose in in vitro and in vivo studies are discussed in detail in (Dineen, P., 1976).

Obtaining oxidized cellulose (monocarboxycellulose) for use in medical practice as a hemostatic agent is carried out by oxidizing cellulose and its derivatives with nitrogen dioxide (NO_2) or nitrogen tetroxide (N_2O_4) in the gas phase and in organic solvents (Kumar, V., & Yang, T., 2002). The duration of the oxidation process and the quality of oxidized cellulose depend largely on the oxidation conditions: the concentration of nitrogen dioxide, the temperature and duration of the process, the state of aggregation of the oxidizer (gaseous or liquid), the nature of the solvent used, and the type of material being oxidized.

The method of oxidation with NO_2 in the gas phase is superior to other methods because the fibrous properties of the product are preserved, but the long duration of the reaction is considered its drawback. Based on this, the purpose of this study was to reduce the reaction time by optimizing the oxidation reaction of viscose fabric in the gas phase of NO_2, as well as to study the structure, properties of the obtained samples.

Materials and Methods

The object of the study was a textile material obtained from a viscose thread by interlacing a satin stitch with a dressing of modified yarn 8.4 tex. We also used reagents NaOH, CCl_4, NO_2, $(CH_3COO)_2Ca$, HCl, bromothymol blue, etc., chemical grade and pure for analysis. All studies used bidistilled water.

Oxidation of viscose fabric

Method 1. 2 g of viscose fabric was taken and placed in a reactor with a volume of 1 liter. Next, the required amount of gaseous NO_2 was fed into the reactor. The oxidation reaction took place at a temperature of 20 °C at different time intervals (6–60 hours). After completion of oxidation, the modified viscose fabric was washed with water to pH 4–4.5, dehydrated using vacuum, treated with isopropanol: water in a 1:1 volume ratio, then with acetone, and dried at 50 °C. The moisture content of the final product was determined (10% ± 2).

Method 2. The viscose fabric was treated with CCl_4 solvent prior to oxidation. For this purpose, the viscose fabric was immersed in a beaker containing CCl_4 for 30 minutes. Subsequently, the viscose fabric was gently squeezed and placed into the reactor. The subsequent process continued according to the procedure described in Method 1.

Determination of the degree of oxidation

The degree of oxidation (DO) of the samples was determined by calcium acetate with minor changes in accordance with USP. Samples (0.2 g preliminarily dried to an absolutely dry state) were placed in a flask with a ground stopper filled with 20 ml of a prepared 0.25 M aqueous solution of $Ca(CH_3COO)_2$, kept on a laboratory shaker (560 rpm) for 6 h

at room temperature. The samples were then titrated with 0.05 N. NaOH solution. Indicator – bromothymol blue. The carboxyl group content was calculated according to the following equation: (1) (Tarbuk, A., Grgich, K., Toshikj, E., Domovich, D., Dimitrovski, D., Dimova, V., et al., 2020).

$$COOH(\%) = \frac{N \times V \times MW(COOH)}{m} \times 100 \quad (1)$$

where N is the normality of the 0.1 M NaOH solution; V is the volume of NaOH consumed, corrected for the blank solution (mL); m is the mass of the sample (mg); MW (COOH) is the molecular weight of the carboxyl group.

FTIR spectroscopy

The infrared spectra of the samples were recorded on an IRTracer-100 infrared Fourier spectrometer (Shimadzu Corp., Japan) complete with a MIRacle-10 frustrated total internal reflection (ATR) attachment with a diamond/ZnSe prism (spectral range on the wavenumber scale is 4000 ÷ 400cm^{-1}; resolution – 4 cm^{-1}).

Morphology of oxidized viscose

The morphology of the structural elements of the samples of oxidized viscose was studied by scanning electron microscopy (SEM). To obtain electronic images, the presented samples were coated with a 10 nm thick silver layer in vacuum using a Q 150 RES device (QUORUM, USA), then analyzed using an EVOMA10 scanning electron microscope (Zeiss, Germany). Microscope extension 10––50 mm, operating voltage 20 kV. Images were obtained using software (SmartSEM).

Hydrolytic degradation *in vitro*

The degree of viscose degradation of samples oxidized viscose samples under in vitro conditions was determined by weight loss in a phosphate buffer solution. To do this, 0.5 g of oxidized viscose with different content of -COOH groups (accurate weight in terms of 100% of the substance) was placed in 50 ml of a phosphate buffer solution at pH 7.4 and a temperature of 36±1 °C. After incubation in a buffer solution for 1–7 days, the samples were quantitatively separated from the solution on a glass filter (with a pore size of 100 μm), thoroughly washed with distilled water to remove sodium phosphates, and dried at 50 °C under vacuum. The sample weight loss Δm, % was calculated using the following equation: (2) (Bychkovsky, P., Yurkshtovich, S et al., 2019).

$$\Delta m = \frac{m_0 - m}{m_0} \quad (2)$$

where, m_0 is the initial mass of the oxidized viscose; m is the mass of the dry samples of the oxidized viscose after being in a phosphate buffer solution.

Results and discussion

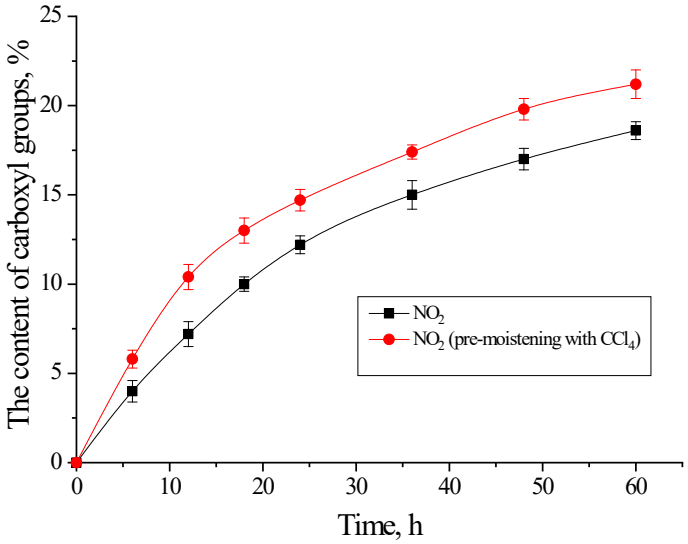
From previous studies, it is known that the oxidation process of cellulose begins with the removal of one hydrogen atom from the cellulose molecule by unpaired electrons in the NO_2 molecule and the formation of Cel-C(•) H-OH. The release of NO• and HNO_2 from the intermediate products formed as a result of the subsequent attack of NO_2• leads to the formation of Cel-CH(OH)$_2$ and Cel-CH O. In the next stage, the elimination of HNO_2 and the subsequent attack of NO_2• leads to the formation of Cel-COOH from Cel-CH(OH) 2. In the case of Cel-CHO, the intermediate product formed as a result of hydrogen evolution and NO_2• attack is first hydrolyzed and Cell-COOH is formed (Mognonov, D.M., Morozov, S.V., Ayurova, O.Z., Chernyak, E.I., Rodionov, V.I., Grigor'eva, M.N., et al., 2019).

Based on the fact that the hemostatic properties of woven materials depend on the structure and type of weaving, we used a material obtained from viscose in the with a dressing of modified yarn 8.4 tex.

When studying the dependence of the oxidation state on the reaction duration under constant temperature and the amount of oxidizing agent, it was established that increasing the reaction time leads to an increase in the DO value of the product. In particular, increasing the reaction duration from 6 to 60 hours led to an increase in the DO values of the products from 4% to 18.6% in the 1st method and from 5.8% to 21.2% in the 2nd method. These studies showed that the oxidation state of the products by the pre-moistening method with CCl_4 is relatively high (Fig. 1). In the oxidation process, the uniform penetration of oxidizing molecules between viscose macromolecules is a very

important process. Because the structural elements of viscose are very densely packed, the penetration of the oxidizing agent is somewhat difficult. The introduction of the oxidizer between the viscose macromolecules, mediated by CCl_4, contributes to the sufficient oxidation of the inner parts of the samples.

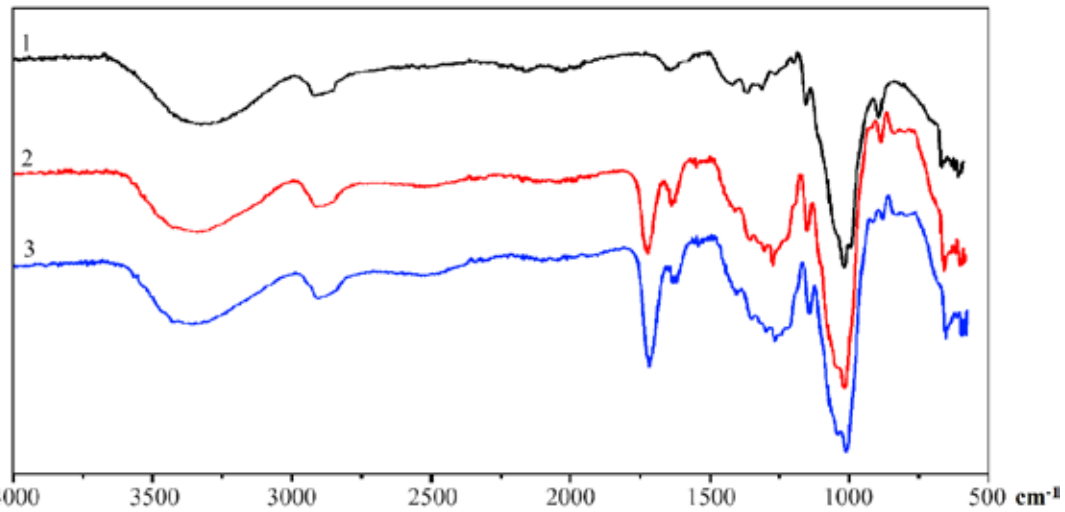
Figure 1. *Dependence of the the content of oxidized viscose carboxyl groups on the oxidation time*



In oxidation experiments with this method, since the samples were moistened with CCl_4 before the reaction, the macromolecule swells in the solvent, and during the oxidation process, by dissolving the oxidizer in itself and accumulating at a high concentration, it facilitates the diffusion of nitrogen dioxide into the inner parts of the viscose. As a result, the oxidation state of the samples is relatively high, and the distribution of carboxyl groups throughout the macromolecule is uniform.

Further studies were devoted to the study of the structure of the obtained samples. The following changes were observed in FTIR-spectra (Fig. 2).

Figure 2. *FTIR spectra of samples (1-viscose, 2-oxidized viscose DO=12%, 3-oxidized viscose DO=15%)*

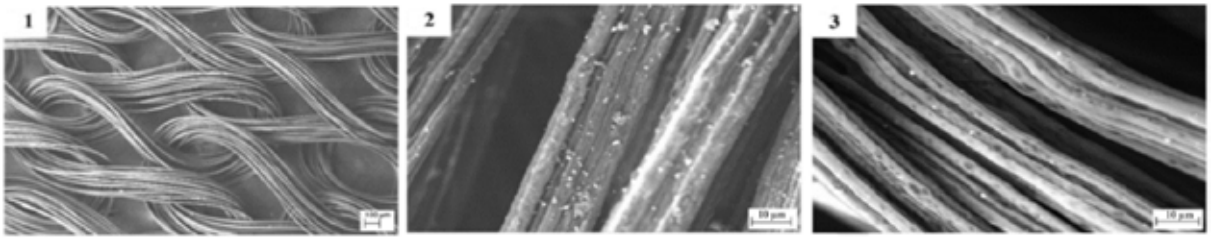


As can be seen from Figure 1 above, an intense absorption band was observed in the FTIR spectrum of oxidized viscose at approximately 1735 cm^{-1}, which corresponds to the -COOH groups in the macromolecule, the intensity of which increases with an in-

crease in the number of carboxyl groups. The main peak located about 3400 cm^{-1} in the oxidized viscose spectrum corresponds to the stretching vibration of the hydroxyl group, and the peaks at 2890 and 1060 cm^{-1} are associated with the stretching bands of $-CH_2$ and –COO (Xu, Y., Qiu, C., Zhang, X., & Zhang, W., 2014). As can be seen, during the interaction of viscose with nitrogen dioxide, the oxidation of primary hydroxyl groups occurs with the formation of carboxyl groups.

Morphological studies have shown that with a relatively low content of carboxyl groups in oxidized samples, the surface microstructure of the fiber practically does not differ from the structure of non-oxidized samples. Identical folded patterns were observed in the viscose samples before oxidation. No cracks were found on its surface. In samples with an oxidation state of 12 and 15%, due to some relaxing effects, delamination of the fibrillar layers of the secondary wall occurred. As a result, cracks were observed on the surface of the fiber's microfibrils (Fig 3.).

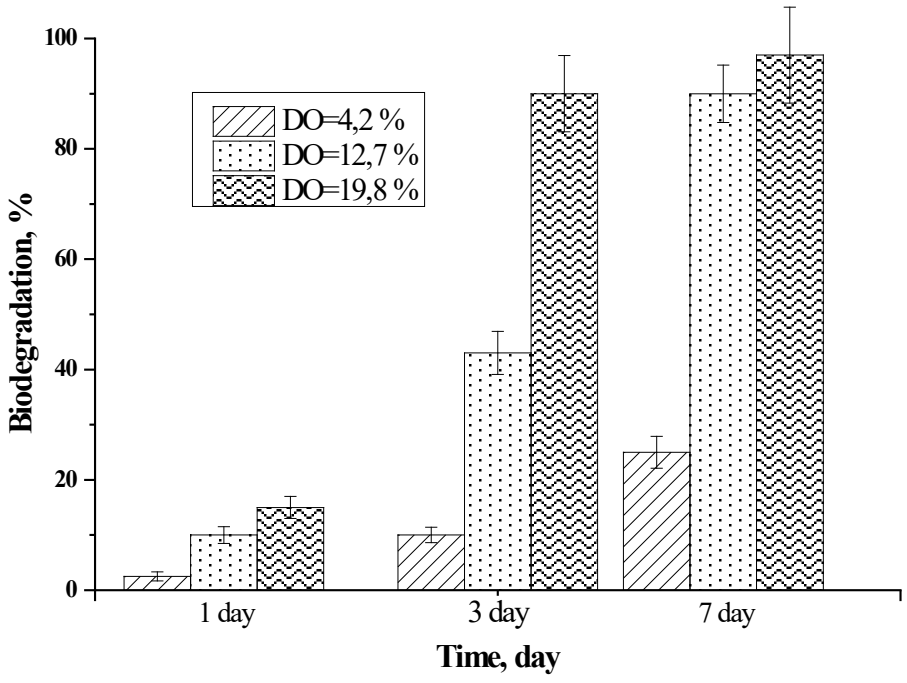
Figure 3. *SEM images of samples (1-viscose, 2-oxidized viscose DO=12%, 3-oxidized viscose DO=15%)*



As a result of SEM analysis, it can be said that the characteristic changes in the morphological structure of viscose fiber, as well as the depth of the structural transformation process, are associated with the degree of oxidation of the samples. The higher the oxidation state, the more cracks and irregularities appear on the surface of the fibers.

In subsequent studies, the decomposition of oxidized viscose under in vitro conditions was studied, in which the degree of decomposition of the samples was determined by weight loss in a phosphate buffer solution (fig. 4).

Figure 4. *Study of the degree of degradatation of samples*



Studies have shown that the decomposition rate of the samples in a phosphate buffer solution increases with increasing oxidation states. A sample with an oxidation state of 19.8% completely decomposed within 3 days, while a sample with an oxidation state of 12.7% decomposed within 7 days. The sample with an oxidation state of 4.2% is more resistant to the decomposition process, and the duration of hydrolysis reaches 40 days.

Conclusion

Thus, the results of studies on the oxidation of viscose with NO_2 showed that when viscose is oxidized by preliminary wetting with gaseous nitrogen dioxide, oxidized viscose with a high content of carboxyl groups (21.2%) is obtained. When studying the structure of the obtained samples by FTIR spectroscopy, it was confirmed that -COOH groups are formed in the macromolecule. Morgological studies also revealed that the fibrous structure of the samples was preserved, and changes in the surface were associated with the content of -COOH groups. Based on the results of research on the decomposition of oxidized viscose, it can be said that the main factor influencing the decomposition rate of oxidized viscose is the content of carboxyl groups.

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