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ESTERIFICATION OF PVA WITH CHLOROANHYDRIDES OF ANHYDRIDE-CONTAINING ROSIN AND SYNTHESIS OF MODIFIERS AS BIOCIDAL ADDITIVES

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Abstract. The esterification reaction of polyvinyl alcohol with chloroanhydrides of the anhydride-containing rosin has been carried out. By interaction of unsaturated cyclic anhydrides – maleic anhydride, anhydride of cis-4-cyclohexene-1,2-dicarboxylic acid and anhydride of bicyclo-[2.2.1]-hept-2-en-5,6-dicarboxylic acid with rosin on the Diels-Alder reaction the corresponding anhydride-containing rosin adducts have been obtained. Further, they by the reaction with thionyl chloride have been converted into the corresponding chloroanhydrides. As a result of the esterification of PVA, the polyesters with yield up to 52%, capable to be hydrolyzed and passed into a water-soluble form have been synthesized. The esterified PVA samples have been tested for the ability to decelerate the growth of mold fungi. It has been shown that the obtained polyesters-modifiers with degree of substitution of 15-20% are able to suppress the growth of mold fungi better than PVA films containing copper naphthenate. The thermal properties of esterified PVA samples has been studied.

Keywords: *Polyvinyl alcohol, anhydride-containing rosin, modifier, esterification, Schotten-Bauman method, antibacterial properties.*

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1. Introduction

The polymers containing double bonds and reactive functional groups in macromolecules are widely used in various branches of the technique - in electronics, in polygraphia, in materials with nonlinear optical properties, etc. Under the action of UV irradiation, these materials are easily cross-linked and therefore can be used, for example, as photoresists (Voitekunas *et al*., 2002; Bulgakova *et al*., 2004). The materials cross-linked due to double bonds of macrochains and reactive groups and the products made on their basis are differed with their reliability and resistance to the action of the external environment. In spite of this, the macroscopic fungi, bacteria, yeast and other microorganisms, acting on products, cause the biological damage of their surface, changing the structural and functional characteristics up to the complete destruction of the material (Kluev *et al*., 2014). This problem is currently being solved by making of biocidal compositions, which include low-toxic and effective antimicrobial additives. As a result of this approach, the use of toxic compounds of arsenic and other heavy metals is limited and more effective antimicrobial additives are used instead. The used compounds, as a rule, have low resistance to the oxidation and color change under the action of

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atmospheric oxygen (Mymrin, 2013). These compounds also must meet the high requirements on part of prevention of the appearance of an unpleasant odor. The use of soluble antimicrobial polymer materials is also promising. Such compositions are made with use of the natural polymers, for ex. cellulose, with the addition of the antimicrobial compounds. The similar modified polymers show the good compatibility and controllability of migration of the antimicrobial compound from the matrix of the composition (Zhang 2017; Fulzele *et al*., 2004).

One of the widely used water-soluble carbochain polymers is polyvinyl alcohol (PVA). It is a non-toxic, biocompatible and bio-destructible polymer. In addition, PVA has excellent film forming and emulsifying properties. All these properties allow the use of this polymer in the field of pharmaceutics, surgery and cosmetic industry. The hydroxyl groups in PVA macrochain participate in the formation of hydrogen bonds. The availability of these functional groups allows to carry out various polymer-analogous reactions, for example, the esterification reaction, with the aim of giving new practically useful properties to the end products.

One of the natural compounds possessing a wide range of biological activity is the rosin and its derivatives. The investigation showed that in some cases, the rosin and its derivatives exceed the known biologically active compounds on efficiency (Kazakova *et al*., 2010; Bazarnova *et al*., 2019). However, the low solubility of the rosin derivatives in water limits their use due to the complexity of their introduction into the organism. Consequently, for the widespread use of the rosin and its derivatives in medical practice, it is necessary to introduce hydrophilic groups into their molecules, which is possible only by modification (Satturwar *et al*., 2005; Lee *et al*., 2005). Since the rosin is not only the main component of wood-chemical raw materials, it is also widely used in various compositions for fungicidal and bactericidal protection of materials, the preparation of water-soluble forms of the rosin and its derivatives by binding it with covalent hydrolytically labile bond with water-soluble polymer remains an important task. Taking into account the stated one, in this work, the modification of PVA with chloroanhydrides of the anhydride-containing rosin has been carried out and the fungicidal properties of the obtained modifiers have been investigated.

2. Experimental part

For investigation were taken: rosin (T_{sof} =70-75ºC, acidic number – 162.8 mg KOH/g, d=1.06 g/cm^3), polyvinyl alcohol (96% hydrolized, MW ~14000, [η] = 0.374 dl/g, T_g = 83°C, T_m = 190°C).

The IR spectra of the synthesized compounds were taken on the device UR-20 "Specord"- 480 in the field of prisms KBr, NaCl and LiF as the thin films. The PMR spectra were taken on the spectrometer BS-487 (80MHz) of firm “Tesla” in various solvents, the internal standard is hexamethyldisiloxane; the chemical shifts of the signals are given in the scale, δ, ppm.

The thermal stability of the samples was determined on the device Paulik-Paulik-Erdei at a heating rate 2°C/min in the range of temperature 20-500ºC, the samples mass was about 1 g.

The viscosity characteristics of the samples of modifier were determined in Ubbelode viscometer in 0.05 M aqueous Na_2SO_4 solution at temperature 30°C ($K=17.4\cdot10^{-4}$; $\alpha=0.53$).

The fungicidal activity was checked according to GOST 9.049-91. ESZKS. "Polymer materials and their components: Methods of laboratory tests for resistance to mold fungi".

The anhydride-containing rosins have been synthesized according to the similar methodology shown in work (Pirguliyeva, 2022). The chloroanhydrides of adducts were obtained by their interaction with thionyl chloride according to the methodology shown in work (Wolfson, 1964).

Esterification of polyvinyl alcohol with chloroanhydrides of the anhydride-containing rosin

The esterification of polyvinyl alcohol with chloroanhydrides of the anhydride-containing rosin was carried out according to a model reaction on the Schotten-Bauman method (Bey *et al*., 2019; Kogai *et al*., 2014).

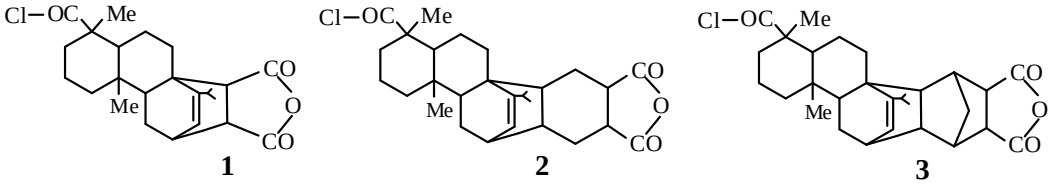
An aqueous solution of PVA (1 mol of PVA in 100 ml of water) was placed in a three-necked flask equipped with a mechanical stirrer, a thermometer and a dropping funnel, at 0°C in an inert gas atmosphere, then an aqueous solution of NaOH (0.5 mol of NaOH in 100 ml of water) and the catalyst of an interphase catalysis – triethylbenzylammonium chloride (TEBA-Cl) was added. After that, a part of chloroanhydride of the anhydride-containing rosin in an organic solvent – mixture of acetone (150 ml) or methyl ethyl ketone with benzene (200 ml) was added dropwise to the solution at intensive stirring. Mixing was continued for 2 h. On completion of the reaction, the organic phase was separated, the aqueous part was extracted twice with sulfuric ether, neutralized with diluted acid (1:10) to a neutral medium, planted in ethanol twice. The precipitate was filtered, washed with ethanol, dried in air at 40°C. Thus, the esterification reaction of PVA with chloroanhydrides of the anhydride-containing rosin has been carried out in the selected conditions, the benzene was used as the organic phase, and TEBA was chosen as the catalyst for interphase transfer.

Hydrolysis of modification products of PVA with chloroanhydrides of the anhydride-containing rosin

The hydrolysis of PVA modified with rosin chloroanhydride was carried out as follows: 10%-s aqueous solution of sodium hydroxide was added to the modifier at 70°C. The reaction was carried out for 0.5 h. After the reaction, the solution was neutralized with diluted solution of hydrochloric acid at room temperature. The polymer was purified by its reprecipitation (twice) into ethanol.

3. Results and discussion

The compounds **1-3** used for the modification of PVA, containing an anhydride group in its molecule are easily obtained on the Diels-Alder reaction from levopimaric acid and unsaturated cyclic anhydrides: maleic (compound **1**), anhydride of cis-4-cyclohexene-1,2-dicarboxylic acid (compound **2**) and anhydride of bicyclo-[2.2.1]-hept-2-en-5,6-dicarboxylic acid (compound **3**). The chloroanhydrides are compounds widely used for preparation of typographic paints, alkyd resins, various binding materials, etc.) (Zhang, 2017).



1 **2** **3**

It was known that the main part (up to 95%) of rosin are various resinous acids and their isomers. The main one is abietinic acid. At the temperature rise to 190-200°C, these acids are converted into levopimaric acid as a result of thermal isomerization – the only isomer, which can undergo the Diels-Alder cycloaddition reactions. Therefore, in a case of carrying out of rosin condensation with the corresponding anhydrides **1-3**, the isomerization of resinous acids occurs firstly and then the anhydride-containing rosin derivatives are formed.

The adducts obtained from rosin and anhydrides had a softening temperatures: 110-115°C (adduct **1**), 116-119°C (adduct **2**) and 117-124°C (adduct **3**) (the used pine pitch rosin had a softening temperature 52-75°C, AN = 170 mg KOH/g).

In the PMR spectra of the synthesized compounds, the proton signals of methyl groups were observed as double doublets in the field of 1.01–1.04 ppm and also the singlet signals in the field of 1.32 ppm, the protons of methylene and methine groups of the condensed cyclic fragments were appeared by multiplet signals in the fields of 0.6 - 1.80 ppm. The methine and methylene protons of the anhydride cycle were appeared by triplet signals in the field of 3.45 ppm and multiplet signals in the fields of 2.20-2.75 ppm, respectively.

In the IR spectra of the compounds **1-3**, the characteristic absorption bands in the field of 1770 cm^{-1}, attributed to the carbonyl groups of the cyclic anhydride fragment and also the absorption bands at 1800 and 1730 cm^{-1} characteristic for chloroanhydride group were observed. The characteristic absorption bands observed at 1440 and 2910 cm^{-1} indicate the presence of methyl and methylene groups, respectively (Figure 1).

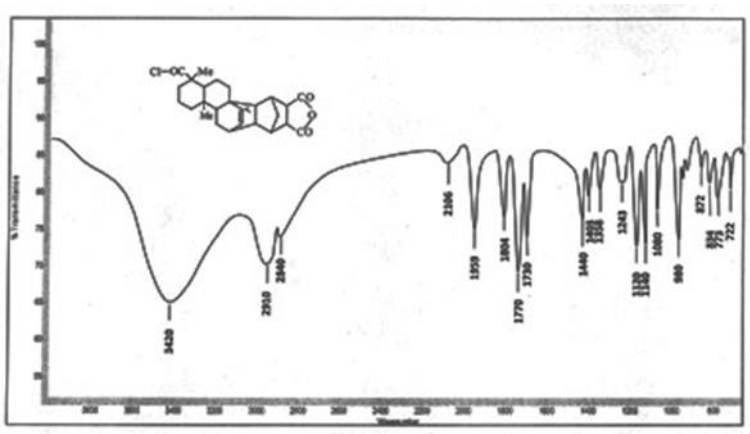
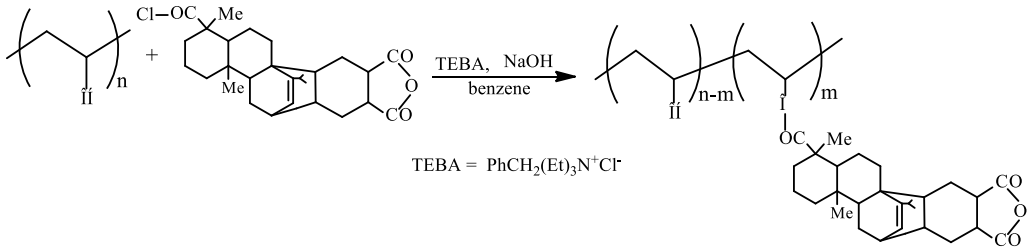


Figure 1. IR spectrum of chloroanhydride of the anhydride-containing rosin **3**

By the PVA reaction with chloroanhydrides **1-3** in the presence of 10% NaOH solution under conditions of interphase catalysis, we have obtained the water-soluble esters on the scheme presented below:



It is accepted that the method of PVA esterification with chloroanhydrides of the organic acids is a well-developed synthetic method for preparation of esters. However, this method also has a number of lacks, one of which is that PVA is not dissolved in organic solvents, and the chloroanhydrides of organic acids are insoluble in water. For this reason, the reaction is carried out in a mixture of solvents. In a case of use of other organic solvents (sulfur ether, ethyl acetate) instead of acetone (or methyl ethyl ketone), the polymer precipitates, i.e. the dissolving ability of water is decreased owing to the insignificant solubility of the used solvents in it. Therefore, the PVA esterification reaction with chloroanhydride we have carried out in water-acetone-benzene solution at 0°C. As a result of the reaction, the modified analogs of PVA were obtained, which are easily dissolved in alcohol. It has been established that the most suitable organic solvent for the carrying out of the esterification reaction is the benzene, and the interphase catalyst – TEBA-Cl. In a case of use of the benzene and TEBA-Cl catalyst as an organic phase in the optimal reaction conditions, the yield of the esterified polymer was ~50%.

For development of the conditions of PVA esterification with chloroanhydrides, the esterification reaction was carried out using the Schotten-Bauman method. For revealing of the optimal conditions of carrying out of the esterification reaction, it was first necessary to find the exact ratio of reagents and the most favorable conditions for carrying out of the reaction. In this case, the molar ratio of chloroanhydride and PVA was changed from 1:5 to 1:10 (based on one elementary link of PVA). The concentration of PVA in water was varied from 4% to 6%. The molar ratio of NaOH: PVA in all cases was constant and corresponded to 1.5. The molar ratio of TEBA-Cl: chloroanhydride in all experiments was constant and equal to 2:3.

It has been found that PVA esterification took place at a molar ratio of the elementary link of PVA: chloroanhydride, equal to 5:1. In a smaller quantity of PVA, the esterification did not occur. Taking into account the advantages of carrying out of reactions in the interphase conditions, the solvents immiscible with water have been chosen as the organic phase. In this case, the highest yield of the purposeful product reached. In increase of PVA concentration in water higher the optimal one (4-6%), the initial polymer precipitated in contact with other reacting components (chloroanhydride, alkali, catalyst).

Since the availability of a hydrogen bond in PVA noticeably decelerates its esterification with chloroanhydrides, the reaction was carried out in an aqueous alkali solution. Namely in these conditions, the reaction proceeds for a short time with sufficiently high degree of substitution. The dependence of a degree of esterification on the reaction duration is shown in Table 1.

Table 1. Degree of esterification of PVA with chloroanhydrides of the anhydride-containing rosin

No	Time, min	Degree of esterification, % Chloroanhydrides of the anhydride-containing rosin		
		1	**2**	**3**
1	10	20	22	23
2	20	38	35	33
3	30	46	42	43
4	60	51	48	48
5	90	52	52	49

In the IR spectra of the modifiers obtained under the above-mentioned conditions, there were absorption bands characteristic for the carbonyl group at 1720 cm^{-1} (the ester fragment), an intensive absorption band at 1170 cm^{-1}, referring to the vibrations of –C–O–C–ether bond, which is characteristic for esters and also small absorption bands at 1800 cm^{-1} and 1730 cm^{-1}, characteristic for chloroanhydride group.

For unambiguous proof of the availability of ester group in PVA macrochain, the modifier was subjected to the hydrolysis reaction. It has been established that in the IR spectra of the hydrolyzed modifier, the absorption bands characteristic for the carbonyl group at 1720 cm^{-1} and the ether bond at 1170 cm^{-1} were absent (Figure 2).

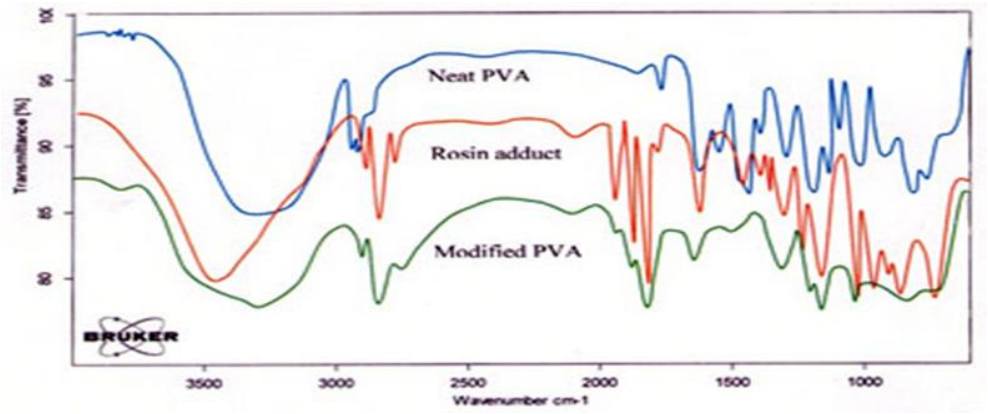


Figure 2. IR spectra of the initial PVA, chloroanhydride of the anhydride-containing rosin – compound **2** and PVA esterified with compound **2**

The study of the thermal properties of PVA samples esterified with chloroanhydrides of the anhydride-containing adducts showed that at heating of the samples in the temperature range 0-250°C, the endothermic peaks corresponding to the glass-transition and melting temperatures are appeared. In Figure 2, TG and DSC curves of pure PVA and modifier with a degree of esterification about 52% are presented, it follows from which that in comparison with initial PVA (T_g =83°C, T_m = 194°C), both the glass transition temperature (T_g=69°C) and the melting temperature (T_m =186°C) are somewhat decreased, possibly due to a decrease of hydrogen bonds between the macrochains of esterified PVA (Figure 3).

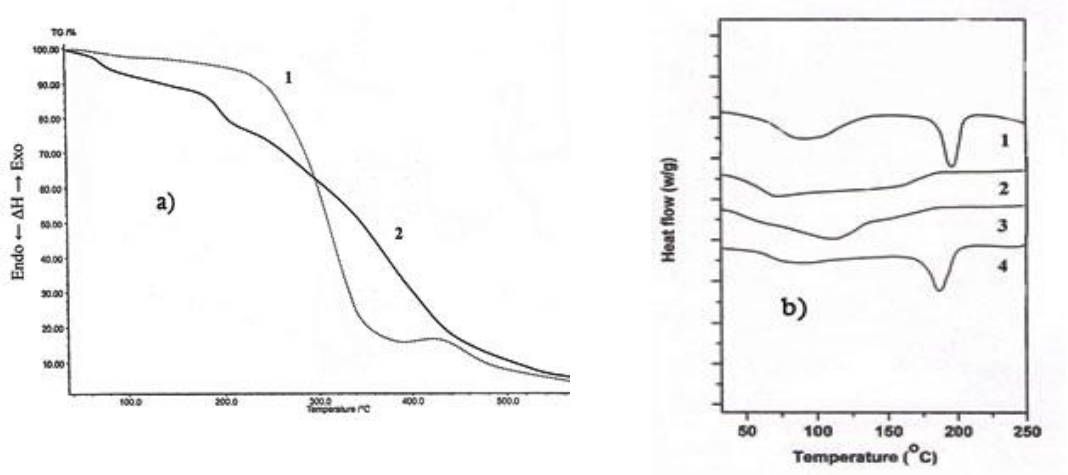


Figure 3. (a) – Thermogravimetric curves of PVA: initial (1), esterified by compound **2** (2); (b) – DSC curves: initial PVA (1), pure rosin (2), compound **2** (3) and PVA, esterified by compound **2** (4)

In TG curves there are kinks corresponding to the temperatures of 64-85°C, 180-210°C and 256°C, which indicates a stepwise decomposition process of a modifier containing volume anhydride groups in the macromolecule chain.

As follows from the data in Table 2, the synthesized modifiers showed the thermal stability up to 180°C. Higher this temperature, the polymers began to decompose intensively. The greatest mass loss (up to 78%) was observed in the temperature range 180-420°C.

Table 2. Results of thermogravimetric analysis and esterified PVA

Temperature, ºC	Initial PVA	PVA, esterified with chloroanhydrides **1-3**		
		1	**2**	**3**
Mass losses, %				
100	2.5	2.3	2.4	2.6
150	4.4	9	11	13
200	5.0	18	21	24
250	16	26	28	29
300	39	36	39	41
350	81	52	52	58
400	85	66	71	78

The characteristic viscosities of the obtained modifiers, determined in 0.05M aqueous solution of sodium sulfate at 30°C, were 0.39-0.41 dl/g.

As noted above, the rosin derivatives have a wide spectrum of antibacterial activity (fungicidal and bactericidal). Moreover, the antibacterial activity of such compounds is combined with their prolonged action. The hydrolyzed modifiers have been tested for the availability of antimicrobial properties in them. For this, the samples as the films made from the obtained water-soluble polyesters have been tested for fungi resistance in accordance with GOST 9.049-91 (State Committee on standards of USSR, 1991). The fungicidal activity of the films was evaluated in points on the degree of fouling of the samples with mold fungi. The obtained indices were compared with the fungicidal

activity of the films of unmodified PVA and the films of PVA with addition of the copper naphthenate.

The tests showed that the PVA films modified with chloroanhydride (degree of substitution 15-20%) show higher fungi resistance (0-1 points) in comparison with PVA films containing copper naphthenate (1-2 points) (Table 3).

Table 3. Fungicidal activity of the samples of compositions on the basis of PVA, modified by chloroanhydrides 1-3

No	Films on the basis of modified PVA	Fungi growth indices in points
0	PVA, modified by chloroanhydride **1**	0-1*
1	PVA, modified by chloroanhydride **2**	0-1*
2	PVA, modified by chloroanhydride **3**	1-2**
3	PVA, modified by copper naphthenate	2-3***
4	Unmodified PVA	3≥****

* – the growth of mold fungi is not observed (under the microscope);
** – the growth of seeds is visible (under the microscope);
*** – the micelles are visible, the growth of seeds is possible (under the microscope);
**** – the fungi growth is clearly visible (under the microscope).

It has been established that PVA analogs esterified with chloroanhydrides of the anhydride - containing rosin have better fungicidal activity in comparison with the used standard fungicide - copper naphthenate.

4. Conclusion

The esterification reaction of PVA with chloroanhydrides of the anhydride-containing adducts of rosin in the conditions of interphase catalysis has been carried out and it has been shown that the reaction proceeds smoothly at 0°C in water-acetone-benzene solution in the presence of TEBA-Cl catalyst. The optimal conditions of carrying out of the esterification reaction of PVA with the compounds **1-3** have been found: the ratio and concentrations of the reacting components, at which the esterification reaction proceeds smoothly with yield up to 52% have been determined. The hydrolysis of esterified products allows to obtain the water-soluble polyesters with side cyclic fragments. The investigation of the thermal properties of the obtained modifiers showed that the introduction of anhydride groups into PVA macromolecule slightly decreases their melting and crystallization temperatures in comparison with the initial PVA. The study of the fungicidal properties of the modifier revealed the availability of antifungal activity in them.

References

Bazarnova, Yu.G., Popova L.M. & Aronova, E. B. (2019). XXI century: Results of the past and the problems of the present, *Journal of the Penza State Technol. University*, 8, 150-154.

Bey, M.P., Puchkova, N.V. & Yuvchenko, A.P. (2019). New adducts of turpentine and rosin with citraconic anhydride and itaconic acid. *Proceedings of the National Academy of Sciences of Belarus, Chemical series, 54*(4), 434–441 (in Russian).

Bulgakova, S.A., Mazanova, L.M., Korsakov, V.S., Novozhilov, A.V. & Lopatin, A.Y. (2004). Chemical amplification resists based on a tert-butoxycarbonyloxystyrene homopolymer and its copolymers with methyl methacrylate. *Polymer Science. Series A*, *46*(6), 657-663.

Fulzele, S.V., Satturwar, P.M., Kasliwal, R.H. & Dorle, A.K. (2004). Preparation and evaluation of microcapsules using polymerized rosin as a novel wall forming material. *Journal of Microencapsulation*, *21*(1), 83-89. https://doi.org/10.1080/02652040410001653768

Kazakova, O.B., Tret'yakova, E.V., Kukovinets, O.S., Tolstikov, G.A., Nazyrov, T.I., Chudov, I.V. & Ismagilova, A.F. (2010). Synthesis and pharmacological activity of amides and the ozonolysis product of maleopimaric acid. *Russian Journal of Bioorganic Chemistry*, 36, 762-770.https://doi.org/10.1134/S1068162010060130

Kluev, A.Y., Skakovskii, E.D., Rozhkova, E.I., Kozlov, N.G., Molchanova, O.A. & Puchkova, N.V. (2014). Synthesis and investigation of antiseptic rosin-based compositions. *Russian Journal of Applied Chemistry*, 87, 230-233. https://doi.org/10.1134/S1070427214020189

Kogay, T.I., Svirskaya, N.M., Ivanchenko, N.M. & Kuznetsov, B.N. (2014). Synthesis of Water-Soluble Polyester by Interaction of Betulonic Acid Chloride with Polyvinyl Alcohol in Conditions of Interphase Catalysis. *Journal of Siberian Federal University. Chemistry*, *7*(1), 79.

Lee, C.M., Lim, S., Kim, G.Y., Kim, D.W., Rhee, J.H. & Lee, K.Y. (2005). Rosin nanoparticles as a drug delivery carrier for the controlled release of hydrocortisone. *Biotechnology Letters*, 27, 1487-1490.https://doi.org/10.1007/s10529-005-1316-x

Mymrin, V.N. (2013). Biopolymers: development prospects. *Polymer Materials*, 11, 36-40 (In Russian).

Pirguliyeva, M.S. (2022). Anhydride-containing rosin and epoxide resins on their basis. *Processes of Petrochemistry and Oil Refining (PPOR)*, *23*(3), 34-45.

Satturwar, P.M., Fulzele, S.V. & Dorle, A.K. (2005). Evaluation of polymerized rosin for the formulation and development of transdermal drug delivery system: a technical note. *AAPS Pharmscitech*, *6*(4), E649-E654. https://doi.org/10.1208/pt060481

State Committee on standards of USSR. (1991). USSR standard: Polymer materials and their components. Methods of laboratory tests for resistance to mold fungi. GOST 9.049-91. Moscow.

United States Patent # US9896537B2. Norbornanyl rosin resin and process for preparing same.

Voitekunas, V.Y., Komarova, L.G., Abadie, M., Rusanov, A.L. & Prigozhina, M.P. (2002). Acylation of hydroxylated poly (imides) by acryloyl chloride and a study of the photosensitivity of the reaction products. *Polymer science. Series A*, *44*(5), 463-467.

Wolfson, N.S. (1964). *Preparative Organic Chemistry*. Moscow.

Zhang, X.C. (2017). *Science and Principles of Biodegradable and Bioresorbable Medical Polymers: Materials and Properties*. Woodhead Publishing, 1-33.