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Functional and Thermal Analysis of Suberin Isolated from Birch Bark

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The functional composition and the process of thermal degradation of suberin samples obtained by water-alkaline and alcohol-alkaline hydrolysis of outer birch-bark were studied by IR-spectroscopy, TGA and DTA methods. It was shown that the partial hydrolysis of birch bark occurs in water-alkaline solution, while alcohol-alkaline hydrolysis of bark yields the mixture of suberinic acids. The alcohol-alkaline suberin destruction occurs at higher temperatures than that of water-alkaline suberin. The basic weight loss is observed at 340-400 °C and 410-440 °C. At these temperatures the loss of weight is 64 % and 91 % for samples of suberin, obtained by water-alkaline and alcohol-alkaline hydrolysis of outer birch-bark accordingly. It was shown that method of suberin isolation from birch-bark defines the composition, properties and areas of the use of suberinic products.

Keywords: suberin, birch-bark outerlayer, water-alkaline and alcohol-alkaline hydrolysis, film-forming materials, binding agent.

The outer bark birch contains up to 35-40 % of pentacyclic triterpenoids with the domination of betulin, which possesses biologically active characteristics. The known ways of the betulin separation are based on the solvent extraction of birch bark, as well as on the birch bark alkaline hydrolysis [1].

The by-product of betulin separation from outer birch-bark is suberin - a complex of hydroxy-acids and phenolic acids, connected with each other by ether and other bonds with the formation of polymeric network.

There is information in literature about perspective trends of suberin and suberinic acid use. It was shown [2] that the mixture of suberinic and phthalic acids are a good glue. Their melts can be used for gluing heated metal. It is also found out that suberinic acids show antibacterial and antifungal activity [3].

There has been investigated the possibility of obtaining film-forming resins by the thermal polycondensation of suberin, separated by the birch bark alkaline extraction. Film-forming materials with technological features similar to those of commercial varnish PF-060 have

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been produced by means of the follow-up dissolution of condensed suberin in styrene and turpentine [4].

The possibility of obtaining fire-proof mixtures on the suberin base has been shown. The impregnation of wood samples with the suberin solution in turpentine, as well as the application of suberin coating makes wood nonflammable material [5].

There have been proposed the methods of production of pressed materials with perfected ecological, physico-mechanical and performance characteristics which have been made of milled wood waste with the use of suberinic binder [6].

The suberin reactivity is determined by the conditions of its extraction from the outer birch bark. So, in order to choose the most rational ways of the suberin use the influence of the extraction methods on suberin composition and its characteristics should be studied.

The purpose of this work is to determine functional composition of suberin samples, produced by the method of alcohol-alkaline and water-alkaline hydrolysis of the outer birch bark and to study their thermo-chemical conversions.

Experimental Part

The water-alkaline suberin was obtained by outer birch-bark hydrolysis in the glass reactor with the volume of 600 ml. 15 g of birch bark (fr. ≥0.315 mm) were loaded into the reactor and 300 ml of 3 % KOH solution were added; the temperature was raised up to 87 °C and the mixture was agitated for 60 minutes. The hot solution was filtered through the cloth filter. The cooled filtrate was acidified by 1 M solution of HCl up to pH = 4-5. The precipitated suberin was filtered and washed on the filter with distilled water till the neutral reaction of washing water. After that the washed sediment was dried in vacuum till the constant weight.

In order to obtain alcohol-alkaline suberin, 300 ml of 40 % KOH solution were added to 15 g (fr. ≥0.315 mm) of birch bark and boiled in the flask with the backflow condenser for 120 minutes. The solution cooled to 70 °C, then 300 ml of isopropyl alcohol were added to the reaction mixture and boiled for 15 minutes. The hot solution was filtered, the isopropyl alcohol was evaporated, the remainder was watered down and betulin was separated by filtering. The water solution was acidified by 1 M solution of HCl till pH =4-5. The precipitated suberin was filtered and washed on the filter with distilled water till the neutral reaction, then it was dried in vacuum till the constant weight.

The elemental analysis of suberin was accomplished with the analyzer Flashe EA™-1112 Thermo Quest (Italia).

The IR-spectra were recorded on the “Spekord 75 JR” in the range of 400 - 4000 cm^{-1}. The samples were mixed and pressed with potassium bromide [8].

Derivatograph “Paulik-Paulik-Erdey-Q-1000D” was used for the thermal analysis in the temperature interval 20 – 800 °C with the heating rate 10 degrees/min. The sample weight was 22.5 mg. The calcined alumina was used as a sample of comparison.

The film-forming polymeric resins were obtained by means of suberin sample polycondensation in the rotating glass reactor with the volume 500 ml in the temperature range 110-220 °C with the retention interval at isothermal conditions for 15 min. Then the thermally treated suberin was cooled till the temperature 20 °C and dissolved in styrene. The conditional viscosity and solubility of suberin samples were estimated [9]. Conditional viscosity of the suberin solution was determined by the viscosimeter with a nozzle diameter 4 mm. The suberin solubility was characterized by the degree of light transmission through the 10 mm cavity on the spectrophotometer"Spekol-4".

For the obtained lacquer compositions on the base of polycondensed water-alkaline and alcohol-alkaline suberin such characteristics, as the film elasticity when bent and the drying up time of coating at the temperature 20 °C were determined according to GOST 28196-89.

For the production of wood plate materials there was used the pine-tree sawdust with fractions < 2.5 mm and 3.8 % mass. humidity. Suberin binding agent and wood filler were carefully mixed in the ratio 30:70 at the temperature 85 °C. Then the produced staff was pressed on the laboratory press under 10 MPa at temperatures 130 – 150 °C.

The wood plate material quality was characterized by density, water-resistance, toughness when statically bent, which were determined according to GOST 10632-89.

The Results and Discussion

The main characteristics of the birch bark suberin samples under investigation are given in Table 1.

The data of Table 1 show that the method of suberin isolation considerably affects both surface appearance and physico-chemical characteristics of the suberin samples. So, atomic ratios H/C and O/C are 1.12 and 0.24 for the water-alkaline suberin, 1.58 and 0.27 for the alcohol-alkaline suberin. The higher ratio H/C and lower melting temperature, probably show lower condensation degree of the alcohol-alkaline suberin in comparison with the water-alkaline one.

IR-spectra of suberin samples, obtained by water-alkaline and alcohol-alkaline hydrolysis of the birch bark are given in Fig. 1. The broad intensive absorption band in the field of 3400-3300 cm^{-1} indicates the presence of the significant amount of hydroxyl groups linked by intermolecular hydrogen bonds in the suberin samples [10]. The absorption band at 1710 cm^{-1} relates to the vibrations C=O bonds in carboxyl and carbonyl groups, the absorption band at 1266 cm^{-1} concerns stretching vibrations C-O bonds in carboxyl groups, bands in the field of 1180-1030 cm^{-1} correspond to the vibrations C-O bond of alcohol groups. The presence of indicated above bands points to the fact that there are different oxygen-containing functional groups in the suberin samples.

IR-spectra of two suberin samples do not have essential differences, except for the small widening of the absorption band in the field of 3400-3300 cm^{-1} of the suberin, isolated by alcohol-alkaline hydrolysis of the birch bark, and the emergence of the additional absorption band at 1128 cm^{-1} related to the stretching vibrations of the simple ether -C-O-C- bonds of the suberin

Table 1. Some characteristics of suberin samples

Characteristics	Water-alkaline suberin	Alcohol-alkaline suberin
Surface appearance	brown powder	brown viscous amorphous substance
Moisture, %	8.3	10.7
Density, kg/m^3	1.15	1.05
Melting temperature, °C	145	118
Elemental composition, %		
C	70.12	67.32
H	6.57	8.84
O	22.37	23.80

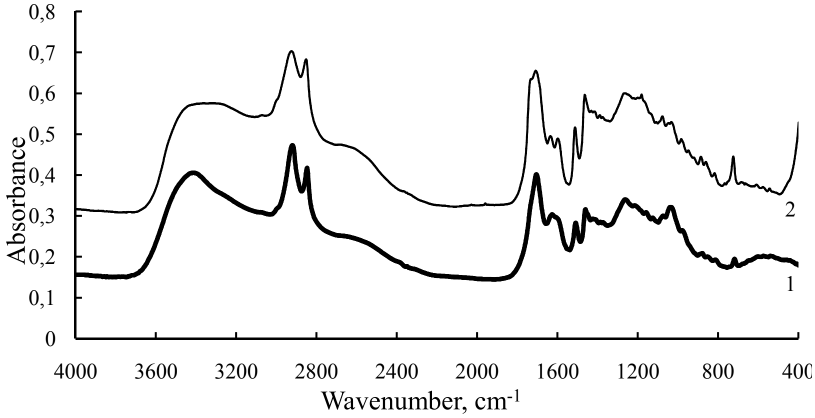

Fig. 1. IR-spectra of suberin samples, isolated from the birch bark by water-alkaline (1) and alcohol-alkaline (2) hydrolysis

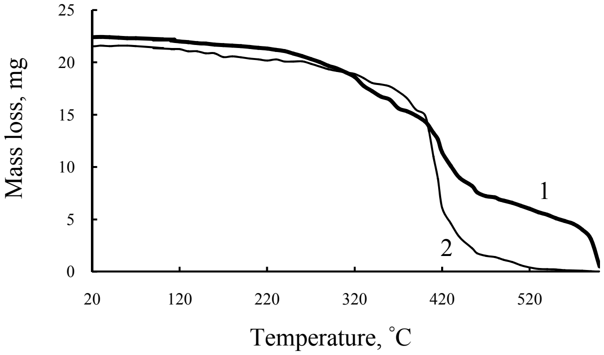

Fig. 2. Thermogravimetric curves of suberin samples, isolated from the birch bark by water-alkaline (1) and alcohol-alkaline (2) hydrolysis

sample, obtained by water-alkaline hydrolysis. Probably, water-alkaline hydrolysis of the birch bark does not result in to the complete destruction of bridge ether links in suberin, while the more deep alcohol-alkaline hydrolysis gives the mixture of suberinic acids. Suberinic acids can undergo the condensation reactions and this fact explains the differences in melting temperature of the samples of water-alkaline (T_{melt}= 145 °C) and alcohol-alkaline (T_{melt}= 118 °C) suberin.

The presence of a high amount of oxygen-containing functional groups in suberin, as well as the low temperature of its softening (65 – 80 °C) makes it worthwhile to use the condensed suberin as a binder agent in the wood plate material production and as a film-forming agent in varnish-and-paint compositions.

The methods of thermogravimetric (TGA) and differential-thermal (DTA) analysis were used in the study of thermal destruction of suberin samples, isolated from the birch bark by water-alkaline and alcohol-alkaline hydrolysis.

The curves of the loss of suberin samples weight with temperature increasing are given on Fig. 2. They show a difference in the thermal behavior of water-alkaline and alcohol-alkaline suberin samples.

As it follows from differential thermogravimetric (DTG) curvers characterizing a rate of mass loss (Fig. 3) the loss of suberin mass goes through a few stages in the temperature

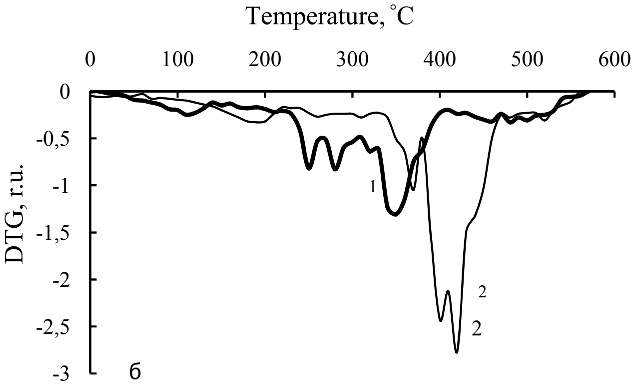

Fig. 3. Differental thermogravimetric curves of suberin samples, obtained from the birch bark by water-alkaline (1) and alcohol-alkaline (2) hydrolysis

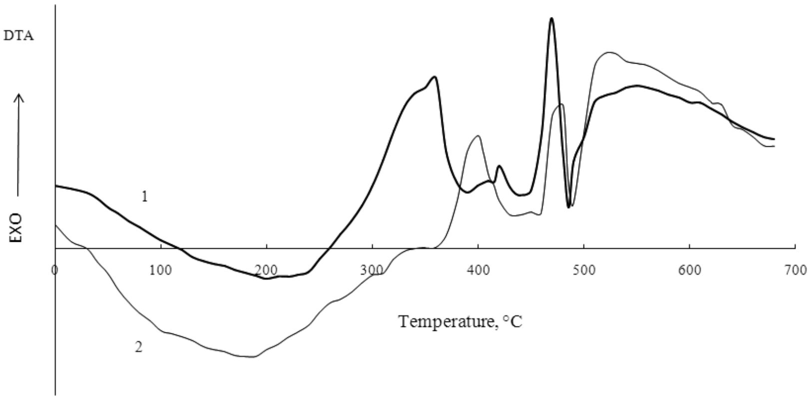

Fig. 4. DTA curves of suberin samples, obtained from outer birch bark by water-alkaline (1) and alcohol-alkaline (2) hydrolysis

range 25-600 °C. The loss of water-alkaline suberin mass with the rise of temperature to 200 °C is only 3.2 %. At the temperature range 200-400 °C the main loss of the water-alkaline suberin (64 % mass.) is observed. The few minimums corresponding to the rate of destruction of water-alkaline suberin are presented on the DTG curve at this temperature range (Fig. 3, curve 1). The presence of low-temperature minimums indicate that in thermodestruction process, at first the rupture of weaker bonds (probably ether and hydrogen bonds) takes place. At higher temperatures the thermal-oxidative degradation of suberin polymeric fragments is carried out.

In the case of alcohol-alkaline suberin the first stage of mass loss (6 %) corresponds to the temperature range 25-340 °C (Fig. 3, curve 2). The further increase of the temperature up to 440 °C is accompanied by the main mass loss of alcohol-alkaline suberin (91 %). The higher temperatures result in the complete combustion both of alcohol-alkaline and water-alkaline samples of suberin.

The differences in the thermal behavior of suberin samples obtained by water-alkaline and alcohol-alkaline hydrolysis of outer birch-bark were observed also by DTA method (Fig. 4).

DTA curve of water-alkaline suberin in the temperature interval 40-260 °C has small endothermal minimum and few exothermal maximums (Fig. 1, curve 1). The first exothermal maximum at 360 °C corresponds to the 45 % mass loss of suberin relative to mass of the initial

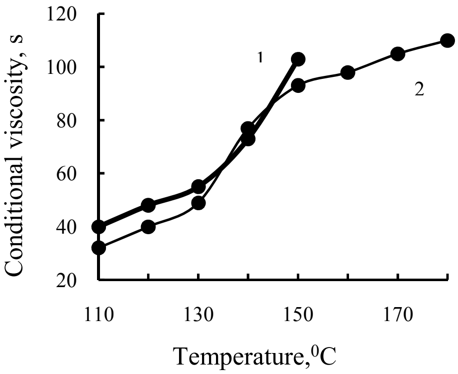

Fig. 5. The temperature dependence of conditional viscosity of thermally condensed water-alkaline (1) and alcohol-alkaline (2) suberin solutions in styrene (25 % mass.)

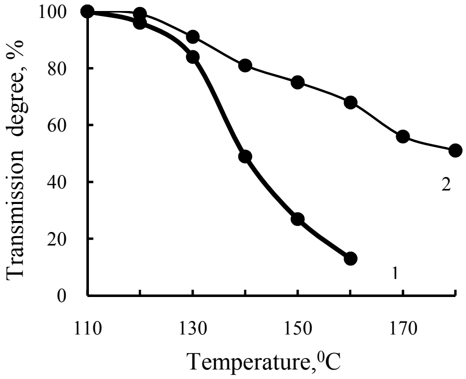

Fig. 6. The temperature dependence of the light transmission degree of thermally condensed water-alkaline (1) and alcohol-alkaline (2) suberin solutions in styrene (25 % mass.)

sample. On the DTA curve of alcohol-alkaline suberin such exothermal maximum is absent. The exothermal maximums at higher temperature probably correspond to reactions of suberin oxidative degradation.

For the alcohol-alkaline suberin the more pronounced endothermal effect is observed in the temperature range 40-360 °C (Fig. 4, curve 2). Obviously, at the lower temperatures of heating (40-200 °C) the desorption of water from suberin samples takes place. The loss of mass of alcohol-alkaline suberin at temperatures 200-360 °C can be explained by reactions of suberinic acids polycondensation.

The results of the accomplished study show that the suberin samples obtained by alcohol-alkaline and water-alkaline hydrolysis of the outer birch-bark possess different functional composition that stipulates for the differences in the processes of their thermochemical conversions. The features of thermal behavior of suberin obtained by different methods define the possible areas of their application for instance in the production of film-forming agent, for varnish-and-paint compositions and of binder for wood plate material.

Fig. 5 and 6 present the results of the temperature influence on some characteristics of suberin samples, obtained by alcohol-alkaline and water-alkaline hydrolysis of the outer birch-bark.

As it follows from Fig. 5, when the temperature raises from 110 °C to 150 °C the conditional viscosity of solutions of condensed suberin samples increases from 40 and 32 to 103 and 93 s for water-alkaline and alcohol-alkaline suberin accordingly. The sample of condensed water-alkaline suberin, treated at 160 °C, practically does not dissolve in styrene, but it swells with the formation of colloidal solution. The increase of condensation temperature of alcohol-alkaline suberin to 180 °C raises the conditional viscosity of styrene solution to 110 s.

As it follows from Fig. 6, the degree of light transmission of solutions of both water-alkaline and alcolhol-alkaline suberin samples condensed at temperatures 110-120 °C decreases insignificantly. The further increase of condensation temperature of water-alkaline suberin to 155 °C leads to the sharp reduction of its solubility. Increasing of the condensation temperature of alcohol-alkaline suberin to 180 °C reduces the degree of light transmission of its styrene solution to 51 %. The polymeric resin sample, obtained by the condensation of alcohol-

Table 2. Main characteristics of varnish compositions, containing suberin rezin (25 % mass.) in styrene solution

Characteristics	Water-alkaline suberin	Alcohol-alkaline suberin	Varnish PF 060
Appearance	Buff, opalescent	Fallow, transparent	Transparent
Conditional viscosity, s	103	93	90
Elasticity when bent, mm	0.7	1.2	1.0
Drying time to Degree 3 at 200 °C, h	46	18	24

Table 3. Influence of pressing temperature on physico-mechanical characteristics of wood plate material

Binding agent*	Pressing temperature, °C	Density, kg/m^3	Bending strength, MPa	Water absorption for 2 hours, %
Water-alkaline suberin	130	621	29	21
	140	664	31	15
	150	745	34	11
Alcohol-alkaline suberin	130	609	27	24
	140	635	35	17
	150	711	31	19

* 30 % relative to mass of press-composition

alkaline suberin at the temperature 215 °C is practically insoluble in styrene.

The water-alkaline and alcohol-alkaline suberin samples, condensed at the temperature 150 °C, were used as film-forming components in varnish compositions, their characteristics are presented in Table 2. For comparison the same characteristics of commercial varnish PF-060 are shown in this table.

The pressing temperature influence on physico-mechanical characteristics of plate material samples, produced in the conditions when the content of suberin binding agent in the press-compositions was 30% mass (Table 3).

The obtained data show that the increase of pressing temperature from 130 °C to 150 °C at the pressure 10 MPa results in the growth of plate materials density (from 609 to 745 kg/m^3), their bending strength and water resistance. When pressing in high temperature, obviously, there occurs the formation of grid-type structures due to the generation of the new chemical bonds (most probably ester ones) between suberin and wood filler and, hence, the physico-mechanical characteristics of wood plate materials are improved.

The use of suberin obtained by alcohol-alkaline hydrolysis of the outer birch-bark as a binding agent, the mechanical strength and water resistance of plate composites have extreme temperature dependence. The wood composite materials, produced at the pressing temperature 140 °C, possess maximum strength properties. The further increase of pressing temperature promotes condensation reactions between suberinic acids; as a result, the part of binder agent does not participate in the wood composite formation. This results in deterioration of the strength property of plate materials.

Based on the accomplished study, there may be given certain practical recommendations on using water-alkaline and alcohol-alkaline suberin. Due to its lower thermal stability, water-alkaline suberin should be used in thermoplastic compositions produced and exploited in the temperature range 40 – 310 °C. Alcohol-alkaline suberin can be recommended for manufacturing the more heat-resistant materials and coating.

Conclusion

The functional composition and the processes of thermal-oxidative degradation of suberin samples obtained by water-alkaline and alcohol-alkaline hydrolysis of outer birch-bark were studied by IR-spectroscopy, TGA and DTA methods. It was shown that the partial hydrolysis of suberinic polymer occurs in water-alkaline solution, while the more complete alcohol-alkaline hydrolysis of outer birch-bark yields the mixture of suberinic acids. The alcohol-alkaline suberin destruction occurs at higher temperatures than that of water-alkaline suberin. The basic weight loss of suberin is observed at 340-400 °C and 410-440 °C. At these temperatures the loss of weight is 64 % and 91 % for samples of suberin, obtained by water-alkaline and alcohol-alkaline hydrolysis of outer birch-bark accordingly. It was shown that the method of suberin isolation from birch-bark determines the chemical composition of suberin samples and their properties. The use of water-alkaline and alcohol-alkaline suberins as film-forming materials and binding agent was suggested.

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