CELLULOSE CHEMISTRY AND TECHNOLOGY

SILYLATION OF PHOSPHORYLATED CELLULOSE

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Received November 15, 2022

In our work, using correlation analysis, we attempted to determine the effect of prior phosphorylation of the substrate with various organophosphorus compounds (OPC) of different nature on the degree of modification of the substrate with organosilicon compounds (OSC). We also tried to determine the dependence of silicon content in % by mass on the temperature and time of modification using the single-factor analysis of variance. It has been established that the pre-phosphorylation of the substrate increases the degree of its modification by the studied OSC. It is most likely due to the fact that polar OPC molecules, which have better penetrating and fixing abilities in the substrate, act as "conductors" of OSC into the substrate structure. The most effective "conductor" of OSC into the substrate, depending on modification time, can be considered tricresylphosphate (TCP) at a modification temperature of 20 degrees, because under these conditions, the correlation coefficients of OSC are higher than for other conditions of OPC processing. Dimethylphosphite (DMP) can be considered the most effective "conductor" of OSC into the substrate depending on the modification temperature because the correlation coefficients for all OSC are higher under these conditions than under other OPC processing conditions. It was found that there was a strong, direct correlation between the time of modification and the percentage of silicon content in the cellulose. The variation in the values of the calculated correlation coefficients ranged from 0.8927 to 0.9827. However, the direct correlation between the modification temperature and silicon content in cellulose in % was stronger and the scatter of correlation coefficients ranged from 0.9719 to 1.

Keywords: cellulose, organophosphorus compounds, organosilicon compounds, dimethylphosphite, trichloroethylphosphite, tricresylphosphate, polyethylhydridsiloxane, tetraethoxysilane, sodium polymethyl siliconate

INTRODUCTION

Cellulose is the main component of materials of plant origin widely used in various areas of human economic activity. Construction is not an exception. It can be explained by the natural origin of plant materials and their harmlessness for the environment and human health. Many composite materials based on cellulose are known.[1-4] However, properties such as low water and fire resistance, as well as susceptibility to biocorrosion, significantly limit the further spread of plant composites in modern construction technologies. An effective solution to this problem is the chemical modification of wood-cellulose materials[5-8] in order to improve their performance. Optimal conditions for cellulose fiber siliconization have been established in a previous study,[9] where different cellulose substrates and organosolv lignin were treated heterogeneously with organic solutions of trialkoxysilanes bearing a variable function on the forth substituent. It was shown for the first time and unambiguously that Si-OR does not react with the hydroxyl groups of cellulose even at high temperature, whereas it condenses with the phenolic OH of lignin. The addition of moisture to these systems induces the partial hydrolysis of the siloxane moieties and the ensuing silanol groups can then react with the cellulose OH, but only at high temperature. Using the latter systems and a siloxane bearing a polymerizable function, it was possible to attach polymethylmethacrylate chains to the surface of cellulose fibres through a two-step procedure. In another paper,[10] it was shown that siloxylation of cellulose makes it possible to reduce the hygroscopicity of the substrate and increase the resistance to the destructive action of water molecules on the cellulose macromolecules. As found by the authors,[10] it becomes possible due to the chemical cross-linking of the siloxane modifier with the hydroxyl groups of cellulose fibers and the formation of polyesters in this way. Other researchers[11] developed a novel method of paper hydrophobization using a new low-cost silicone system based on an emulsion of triethoxymethylsilane in water mixed in a low concentration with a water solution of starch. Thus, satisfactory hydrophobicity (with a water contact angle greater than 90°) could be achieved even with 10 wt% of initial triethoxymethylsilane in 4 wt% starch water solution. The greatest hydrophobization (with a water contact angle greater than 100°) was obtained using starch/siloxane mixtures. A coating based on an aqueous triethoxymethylsilane solution without starch resulted in decreased contact angles and decreased resistance to water. The application of the developed system using the Mayer rod coating method provided hydrophobic properties, with no surface color changes, while also preserving basic mechanical properties, such as tensile strength and tear resistance. Furthermore, the hydrophobized paper samples indicated non-zero air permeance, which qualified them as a breathable material. An increase in the roughness of the coated paper surfaces was also observed.

Previous work[12] shows the effectiveness of organosilicon modifiers not only for hydrophobizing the surface of cellulosic materials, but also for ensuring the strength of the substrate. Poly(methylhydrogen)siloxane (PMHS) was applied for hydrophobic modification of bamboo flour (BF) at room temperature based on the dehydrogenation between hydroxyl groups of BF and –Si–H of PMHS, and the effect of PMHS modification on mechanical properties of BF/HDPE (high-density polyethylene) (BF/HDPE) composites was investigated. It was found that the hydrophobicity of BF was significantly improved by PMHS modification, and the mechanical properties of BF/HDPE composites could be adjusted effectively. According to the results of the research, the tensile strength increased by 34.9% as the weight ratio of 1.5PMHS to BF was 3%. 0.2PMHS modification improved simultaneously the tensile strength and impact strength, probably due to an elastic and hydrophobic 0.2PMHS layer formed on BF surface. The tensile and impact strength increased by 16.9 and 13.1%, respectively, as the weight ratio of 0.2PMHS to BF was 4%.

Phosphorus-containing compounds are added to the composition of the modifiers to provide fire protection for the cellulose. The phosphoramidate siloxane compound can significantly improve the flame retardant properties of cotton fabrics by promoting the formation of a char layer and the release of non-combustible volatiles. The LOI of cotton with 16% of weight gain can reach 30.3%, which is significantly higher than that of the control cotton, and 27.0% of LOI value can be maintained after 20 washing cycles. In addition, this finishing method caused a slight decrease in the tensile strength and breaking elongation for cotton fabrics, which suggests that this kind of flame retardant material has a certain potential in practical applications.[13] Processes of cellulose modification by a mixture of orthophosphoric acid and ammonium polyphosphate in urea medium or the same compositions with magnesium salt addition are described in the literature.[14] It has been shown that under the conditions of modification, the esterifying composition undergoes directed anionic reorganization with the formation of linear short-chain polyphosphates. It has been established that the level of fire resistance of modified cellulose using phosphate compositions depends both on the content of phosphorus in the tissues and on the composition of the introduced ester groups. The efficiency of the obtained materials' fire resistance increases as the length of the phosphate chains increases. The resulting cellulose phosphates have a level of fire resistance consistent with difficult-to-fire materials. Many other scientific studies[15-20] confirm the high efficiency of organophosphate modifiers for fire resistance. In their presence, during the thermal decomposition of cellulose materials, the yield of volatile products decreases, the yield of coke residue increases, and the temperature at the beginning of intensive thermal decomposition decreases. During the thermal decomposition of wood modified with organophosphorus compounds (OPC), free radicals are formed, which participate in recombination reactions with the wood decomposition products. These processes reduce the time for independent combustion and smoldering.[21]

The impregnation of cellulose materials with organosilicon compounds (OSC) presents certain difficulties because OSC are hydrophobic agents.

Impregnation is carried out by the autoclave method, in hot-cold baths with a temperature difference of 65°–20°; the duration of impregnation is at least 7 hours.[22,23] According to another method, the impregnation is carried out at 140 °C for 36 hours.[24] In both cases, such impregnation methods consume a lot of organosilicon compounds and energy. Unlike OSC, organophosphorus compounds have high hydrophilicity and correspondingly high permeability in wood, for example, during surface treatment of wood, dimethyl ester of phosphoric acid (DMP) penetrates to a depth of up to 7 mm.[25] Taking into account the hydrophilic properties of OPC and the hydrophobic properties of OSC, a sequential treatment with OPC and OSC was suggested for wood modification.[26,27]

The examples of modification of cellulose-containing substrates by OSC and OPC described above show high efficiency in terms of improving the performance of the final product. Phosphorylation of cellulosic materials improves fire and bio-resistance, as demonstrated by numerous studies. Additionally, silylation makes the surface of cellulose-based substrates hydrophobic. In this regard, the study of patterns of sequential treatment with phosphorus and organosilicon compounds and the establishment of optimal parameters is a very topical task. It is of scientific interest to study the effect of preliminary phosphorylation of the cellulose substrate on the degree of subsequent silylation, as well as determining the role of the nature of the phosphorylation agent on the yield of the final silylation product. In our work, using methods of correlation analysis, we attempted to establish the influence of OPC phosphorylating agents of different nature on the degree of modification of the OSC substrate. We also tried to determine the dependence of silicon content in percent % by mass on the temperature and time of modification using the single-factor analysis of variance.

EXPERIMENTAL

As modification objects, α-cellulose fibers were used. Modification was carried out under mild conditions by immersion in dilute solutions of OPC: dimethylphosphite (DMP), trichloroethylphosphite (TIT), and tricresylphosphate (TCP); and in dilute solutions of OSC: polyethylhydridsiloxane (PEHS), tetraethoxysilane (TES), and sodium polymethyl siliconate (SPMS). In addition, sequential modification was carried out first with solutions of OPC, then OSC in various combinations. Hexane "ch" was used as an organic solvent for OSC, CCl_4 was used for OPC, while DMP and SPMS were dissolved in water. The concentration of OPC and OSC solutions was 10% by weight, the modification time was 3 hours, and the modification temperature was 25 °C. After each modification step, the samples were extracted for three hours with an appropriate solvent to remove any excess unreacted modifier. The interlayer exposure interval for the sequential modification with OPC followed by OSC and the drying time of the samples was 24 hours.

The silicon content in the samples was determined in accordance with GOST 20841.2, "Organosilicon Products. Methods of determination of silicon content". In accordance with the methodology, a sample of the test product is weighed (the result of weighing is recorded in grams to the fourth digit) in a quartz flask, quartz crucible, or porcelain crucible, preheated in a muffle at 800 °C to a constant weight (tolerable differences between the last two weighings shall not exceed 0.0002 g), into which 25% oleum is poured, along with 2-3 drops of nitric acid, and gently heated on an electric stove. Then, nitric acid is added dropwise to the flask again until the brown vapors stop discoloring, indicating that the oxidation of the organosilicon compounds is complete.

After that, another 2-3 drops of nitric acid are added, and the contents of the flask or crucible are evaporated, intensifying the heating, to remove the excess acid. During heating, no strong foaming should be ensured. At the beginning of foaming, the flask or crucible is removed from the hotplate.

When the evaporation is finished, the flask or crucible is placed in a muffle furnace and incinerated at 800-850 °C for 2 hours. Then, the flask or crucible is transferred into a desiccator, cooled for 30–60 minutes, and weighed (the result of the weighing is recorded in grams to the fourth decimal place). The steps of hardening, cooling, and weighing are repeated until a constant mass is obtained.

The analysis of the experimental data was performed in two stages: at the first stage, the correlation coefficient was calculated to establish the effect of OPC of different nature on the degree of modification of the OSC substrate with regard to temperature and time. The correlation coefficient was calculated using the following formula:

$$r = \frac{n\sum xy - \left(\sum x\right)\left(\sum y\right)}{\sqrt{\left[n\sum x^2 - \left(\sum x\right)^2\right]\left[n\sum y^2 - \left(\sum y\right)^2\right]}} \qquad (1)$$

The resulting correlation coefficient reflects the degree of relationship between the two indicators and also determines the direction of the relationship between the dependent and independent variables. The values of the correlation coefficient range from -1.0 (strong negative relationship) to +1.0 (strong positive relationship). When the correlation coefficient is equal to zero, there is no relationship between the indicators.

In the second stage of the analysis, by methods of single-factor analysis of variance, the effect of OSC processing conditions (temperature and time of modification) on the silicon content in cellulose in % by mass was determined.

When constructing a model of one-factor analysis of variance, the result of the experiment is some random variable X, also called the resultant variable. The values of the random variable X are influenced by the factor A, which consists of several levels (groups) A_j, j = 1,...,k.

We denote by x_{ij} the value of the *i*-th observation ($i = 1,...,n$) in the *j*-th level of factor *A*. Then, the model of one-factor analysis of variance can be represented as follows:

$$x_{ij} = a + m_j + \varepsilon_{ij}\,, \tag{2}$$

where a is the general average of all conceivable observation results, *i.e.*, *M*(*X*), and m_j is the effect on *X* caused by the *j*-th level of factor *A*, or, otherwise, the deviation of the mathematical expectation a_j a of the result indicator at the *j*-th level of factor A from the total mathematical expectation *a*, *i.e.*, $m_j = a_j - a$; ε_{ij} - the random residual reflecting the effect on the value x_{ij} from all other uncontrollable factors.[31]

The sample average corresponding to the *j*-th level of factor *A* (group average) is calculated by the formula:

$$\overline{x_j} = \frac{1}{n}\sum_{i=1}^{n} x_{ij} \tag{3}$$

The arithmetic means of all values or the overall mean:

$$\overline{x} = \frac{1}{nk}\sum_{j=1}^{k}\sum_{i=1}^{n} x_{ij} = \frac{1}{k}\sum_{j=1}^{k}\overline{x_j} \tag{4}$$

The total sum of squares is the sum of squares of the deviations of observed values x_{ij} from the overall mean:

$$Q = \sum_{j=1}^{k}\sum_{i=1}^{n}\left(x_{ij} - \overline{x}\right)^2 = \sum_{j=1}^{k}\sum_{i=1}^{n} x_{ij}^2 - nk\overline{x}^2 \tag{5}$$

Factor sum of squares (due to the influence of factor *A*) is the sum of squares of deviations from the overall mean of group averages:

$$Q_f = n\sum_{j=1}^{k}\left(\overline{x_j} - \overline{x}\right)^2 = n\sum_{j=1}^{k}\overline{x_j}^2 - nk\overline{x}^2 \tag{6}$$

The residual sum of squares characterizes the scatter within the group:

$$Q_o = \sum_{j=1}^{k}\sum_{i=1}^{n}\left(x_{ij} - \overline{x_j}\right)^2 \tag{7}$$

Then, the identity is true:

$$\sum_{j=1}^{k}\sum_{i=1}^{n}\left(x_{ij} - \overline{x}\right)^2 = n\sum_{j=1}^{k}\left(\overline{x_i} - \overline{x}\right)^2 + \sum_{j=1}^{k}\sum_{i=1}^{n}\left(x_{ij} - \overline{x_i}\right)^2 \tag{8}$$

or

$$Q = Q_f + Q_o \tag{9}$$

Thus, the total sum of squares of deviations from the overall mean *Q* is divided into two components: Q_f is the sum of squares between groups, and Q_o is the sum of squares within groups.

The corresponding numbers of degrees of freedom are calculated as follows:

$$v = nk - 1; \qquad v_f = k - 1; \qquad v_o = k\left(n - 1\right) \tag{10}$$

and the variances:

$$\overline{S^2} = \frac{Q}{v}; \qquad \overline{S_f^2} = \frac{Q_f}{v_f}; \qquad \overline{S_o^2} = \frac{Q_o}{v_o}. \tag{11}$$

Note that the value $\overline{S^2} = \frac{Q}{v}$, which is an unbiased estimator for σ^2, will always have a distribution χ^2 with *v* degrees of freedom, and a confidence interval for σ^2 can be constructed from it.[31]

If the null hypothesis of equality of means is true, then these variances are unbiased estimates of the variance of the general population. The difference in the means of the groups can explain a significant excess of variance $\overline{S_f^2}$ over variance $\overline{S_o^2}$. Therefore, to test the null hypothesis, the ratio of these averages *F*-statistics is used, which is called the variance ratio:

$$F = \frac{\overline{S_f^2}}{\overline{S_o^2}} = \frac{\dfrac{Q_f}{k-1}}{\dfrac{Q_o}{k\left(n-1\right)}}, \tag{12}$$

which has a Fisher distribution with (*k* - 1) degrees of freedom and (*n* - 1). The null hypothesis does not contradict the results of observations at a given significance level α, if:

$$F < F_U\left(k-1, k\left(n-1\right)\right) \tag{13}$$

in this case, it is assumed that factor *A* does not have a significant effect on the indicator *X*.

For a given significance level α, the null hypothesis is rejected if the calculated F-statistic is greater than the upper critical value of F_U. Thus, as shown in Figure 1,[32] the decisive rule is formulated as follows: the null hypothesis H_0 is rejected if $F > F_U$, in which case factor *A* is considered to have a significant effect on the index *X*.[32]

If the null hypothesis H_0 is true, the calculated *F*-statistic is close to 1, since its numerator and denominator are estimates of the same value—the variance σ^2 inherent in the analyzed data. If the null hypothesis H_0 is false (and there is a significant difference between the mathematical expectations of different groups), the calculated *F*-statistic will be much larger than unity, since its numerator $\overline{S_f^2}$, in addition to estimating the natural variability of the data, estimates the effect of experimental conditions or the difference between groups, while the denominator $\overline{S_o^2}$ estimates only the natural variability of the data.[32]

RESULTS AND DISCUSSION

Previously published research[21] describes the main results obtained in the phosphorylation of cellulose with phosphoric acid esters, substituted phosphoric acid amides, phosphinic acids, and oligophosphazenes. In the IR spectra of phosphorylated cellulose, the appearance of absorption bands in the region of 1095 cm^{-1} and 1236 cm^{-1}, which corresponds to pentavalent phosphorus, was found. The degree of substitution presented in Table 1 depends on the nature of the organophosphorus modifier and the modification temperature and can reach 2.8%.

The data in Table 1 show that for all organosilicon modifiers, prior phosphorylation of the substrate increases the degree of modification. Increasing the exposure time and temperature also leads to an increase in the percentage of silicon in the composition of the substrate. The data on the percentage of silicon in the composition of the modified substrate (Table 1) show that pre-phosphorylation with DMP allows for the inoculation of more organosilicon modifier compared to other OPC.

Table 2 shows the calculated correlation coefficients of the dependence of OPC treatment conditions (no OPC, DMP, TIT, TCP) on silicon content in cellulose for 4 hours. For each OSC treatment condition (SPMS, TIT, PEHS), these coefficients are calculated for three temperatures of 20, 40 and 60 degrees.

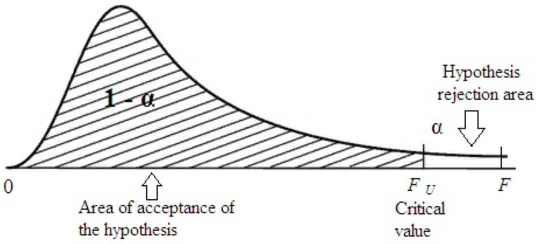


Figure 1: Critical area of the analysis of variance when testing hypothesis H_0

Table 1
Elemental analysis for silicon and modified cellulose samples

№	Processing conditions			P content,[21]	Si content, wt%			
	OPC	OSC	T, °C	wt%	1 h	2 h	3 h	4 h
1	-----	SPMS	20	--	1.75	2.30	2.55	2.60
			40	--	2.40	3.10	3.35	3.40
			60	--	3.40	4.07	4.26	4.30
			80	--	4.30	4.84	5.19	5.21
2	DMP	SPMS	20	0.9	2.90	4.40	4.80	4.90
			40	1.4	4.20	5.60	6.17	6.20
			60	2.2	5.40	6.80	7.38	7.41
			80	2.8	6.70	8.40	8.78	8.80
3	TIT	SPMS	20	0.2	1.40	2.20	2.55	2.60
			40	0.3	1.65	2.40	2.77	2.80
			60	0.3	1.80	2.58	3.00	3.10
			80	0.4	2.00	2.68	3.10	3.20
4	TCP	SPMS	20	0.2	0.70	1.00	1.26	1.30
			40	0.25	0.88	1.21	1.40	1.41
			60	0.3	1.06	1.45	1.60	1.65
			80	0.35	1.22	1.66	1.88	1.90
5	-----	TES	20	--	0.34	0.50	0.73	0.75
			40	--	0.55	0.70	0.92	0.95
			60	--	0.74	0.88	1.11	1.14
6	DMP	TES	20	0.9	0.50	0.72	0.93	0.96
			40	1.4	0.65	0.81	1.10	1.13
			60	2.2	0.80	1.03	1.28	1.30
7	TIT	TES	20	0.2	0.40	0.59	0.76	0.80
			40	0.3	0.60	0.78	0.95	1.00
			60	0.3	0.80	1.00	1.20	1.25

8	TCP	TES	20	0.2	0.53	0.55	0.56	0.57
			40	0.25	0.62	0.67	0.69	0.70
			60	0.3	0.71	0.77	0.79	0.80
9	-----	PEHS	20	--	0.03	0.08	0.14	0.14
			40	--	0.12	0.17	0.22	0.23
			60	--	0.20	0.27	0.31	0.33
10	DMP	PEHS	20	0.9	0.07	0.16	0.26	0.28
			40	1.4	0.21	0.32	0.43	0.44
			60	2.2	0.35	0.45	0.55	0.57
11	TIT	PEHS	20	0.2	0.13	0.23	0.33	0.35
			40	0.3	0.26	0.40	0.50	0.52
			60	0.3	0.41	0.52	0.64	0.65
12	TCP	PEHS	20	0.2	0.06	0.14	0.23	0.24
			40	0.25	0.15	0.25	0.35	0.36
			60	0.3	0.25	0.35	0.46	0.47

Table 2
Correlation coefficients of the dependence of different OPC's effect on the degree of modification of OSC substrate (silicon content in cellulose in % at time of 1, 2, 3 and 4 h)

Processing condition	SPMS			TES			PEHS		
	20°	40°	60°	20°	40°	60°	20°	40°	60°
no OPC	0.9282	0.9106	0.8942	0.961	0.9671	0.9664	0.9473	0.9683	0.9676
DMP	0.8927	0.9056	0.9067	0.96	0.9627	0.9568	0.9707	0.9562	0.9683
TIT	0.9199	0.9215	0.9432	0.9683	0.9752	0.973	0.9683	0.9556	0.9573
TCP	0.959	0.9276	0.9276	0.9827	0.9431	0.9287	0.9613	0.9573	0.9584

Table 3
Correlation coefficients of the dependence of different OPC's effect on the degree of modification of OPC substrate (silicon content in cellulose in % at 20, 40 and 60 degrees)

Processing condition	SPMS				TES				PEHS			
	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h
no OPC	0.9926	0.9985	0.9993	0.9994	0.9996	0.9995	1	0.9999	0.9994	0.9995	0.9994	0.9995
DMP	0.9997	1	0.9994	0.9998	1	0.9719	0.9997	1	1	0.9982	0.9951	0.9982
TIT	0.9897	0.9995	0.9999	0.9934	1	0.9991	0.9969	0.9979	0.9992	0.9951	0.9984	0.9971
TCP	1	0.9993	0.9948	0.9778	1	0.9986	0.9972	0.9972	0.9995	0.9996	0.9997	0.9997

Table 2 shows that all values are quite close to 1, so we can conclude that there is a strong direct correlation between the time of the experiment and the silicon content. A scatter of values is noted for the calculated correlation coefficients in Table 2 from 0.8927 to 0.9827. Depending on the value of the correlation coefficient, we can see for which conditions of OPC treatment it will be stronger, for example, at 20 degrees, for the conditions of TCP treatment for all OSC (SPMS, TES, PEHS), the correlation coefficients will be higher than for other conditions of OPC treatment: no OPC, DMP, and TIT. At the other temperatures, there was no special scatter in the correlation coefficient, so approximately the same degree of correlation was obtained in each experiment.

Let us calculate correlation coefficients of the influence of OPC treatment conditions: no OPC, DMP, TIT, TCP on silicon content at different temperatures from 20 to 60 degrees. These coefficients were calculated for modification times of 1, 2, 3, and 4 hours for each OSC treatment condition: SPMS, TES, and PEHS.

Having compared the obtained correlation coefficients (Table 3) with the obtained correlation coefficients in Table 2, we can conclude that there is a strong direct relationship between the modification temperature and silicon content, and this relationship is stronger than the relationship of silicon content in cellulose with modification time (as seen from the calculated values of the correlation coefficient). In this table, the scatter of correlation coefficient values is less than in Table 2, where the minimum value of the correlation coefficient is 0.9719 and the maximum is 1. It can be concluded that the lowest value of the correlation coefficient is achieved for the conditions of DMP processing at a time of 2 hours for all OSC processing conditions (SPMS, TES, PEHS) and for the conditions of TCP processing at a time of 4 hours for all OSC processing conditions.

The next stage of the analysis of the experimental data involved applying the method of single-factor analysis of variance, which is the most productive method designed to evaluate the impact of various factors on the experimental result.

The null hypothesis H_0 is tested for each OSC processing condition: $m_1 = m_2 = ... = m_k$ about the absence of its influence on the result indicator X (silicon content in % of cellulose) of the factor A (task 1 – time, task 2 – temperaturee), which has k levels $A_j, j = 1,...,k$.

The main idea of variance analysis is to compare the variance due to the influence of factor A with the variance due to random causes. If the difference between them is insignificant, then the influence of factor A on trait X is also insignificant. If the difference between factor and residual variance is significant, then it indicates the influence of factor A on the trait X under consideration. It is assumed that the random variable X has a normal distribution with mathematical expectation m_j, which depends on the level of factor A_j, and a constant variance σ^2. As the initial data, we use sample values of X obtained experimentally for each factor A (time and temperature). The number of sampling elements at each level is n, and the total number of observations is n_k.

Let us determine the dependence of silicon content in % on the conditions of OSC processing at a certain temperature. We use the data in Table 1. For the three temperatures: 20 °C, 40 °C, and 60 °C, four values of silicon content in % are presented in each group for one condition of OSC treatment. The groups are divided by time: 1 hour, 2 hours, 3 hours and 4 hours. The results of the calculations performed by the methods of one-factor analysis of variance for each type of OSC treatment condition are introduced into Tables 4-6.

The P-value in Tables 4-6 shows the probability that, under the true null hypothesis, the F-statistic is not less than the calculated value.

Table 4
Results of one-factor analysis of variance for SPMS treatment condition

T, °C	Source of variance	Sum of squares	Nr degrees of freedom	Variance	Fisher's statistics, F	P-value	F_U
20°	Between groups	3.43051875	3	1.14350625	0.631028382	0.60891994	3.490294819
	Within groups	21.745575	12	1.81213125			
	Total	25.1760937	15				
40°	Between groups	3.561075	3	1.187025	0.350956338	0.789259408	3.490294819
	Within groups	40.5871	12	3.382258333			
	Total	44.148175	15				
60°	Between groups	3.674475	3	1.224825	0.231859892	0.872434541	3.490294819
	Within groups	63.3913	12	5.282608333			
	Total	67.065775	15				
80°	Between groups	3.863625	3	1.287875	0.155313569	0.924245567	3.490294819
	Within groups	99.50515	12	8.292095833			
	Total	103.368775	15				

Table 5
Results of one-factor analysis of variance for TES treatment condition

T, °C	Source of variance	Sum of squares	Nr degrees of freedom	Variance	Fisher's statistics, *F*	*P*-value	F_U
20°	Between groups	0.27756875	3	0.092522917	5.65961514	0.011866676	3.490294819
	Within groups	0.196175	12	0.016347917			
	Total	0.47374375	15				
40°	Between groups	0.303475	3	0.101158333	6.018344075	0.009629045	3.490294819
	Within groups	0.2017	12	0.016808333			
	Total	0.505175	15				
60°	Between groups	0.33735	3	0.11245	3.977597642	0.035139742	3.490294819
	Within groups	0.33925	12	0.028270833			
	Total	0.6766	15				

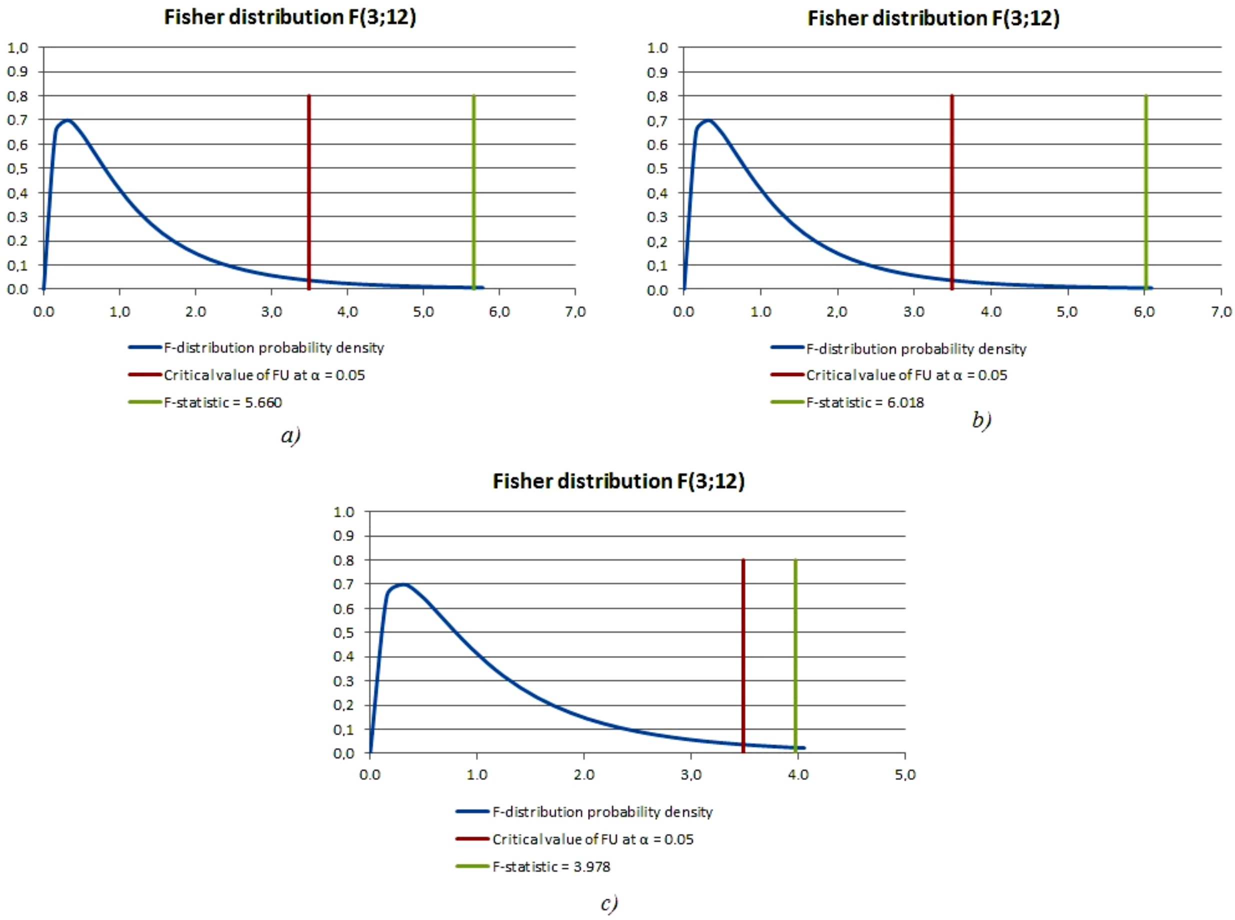


Figure 2: Fisher distribution for TES treatment conditions of temperature: (a) 20 °C, (b) 40 °C, (c) 60 °C

Table 6
Results of one-factor analysis of variance for PEHS treatment condition

T, °C	Source of variance	Sum of squares	Nr degrees of freedom	Variance	Fisher's statistics, *F*	*P*-value	F_U
20°	Between groups	0.08466875	3	0.028222917	5.796747967	0.010946523	3.490294819
	Within groups	0.058425	12	0.00486875			
	Total	0.14309375	15				
40°	Between groups	0.10586875	3	0.035289583	3.263147756	0.059335512	3.490294819
	Within groups	0.129775	12	0.010814583			
	Total	0.23564375	15				
60°	Between groups	0.105525	3	0.035175	2.346955796	0.124184706	3.490294819
	Within groups	0.17985	12	0.0149875			
	Total	0.285375	15				

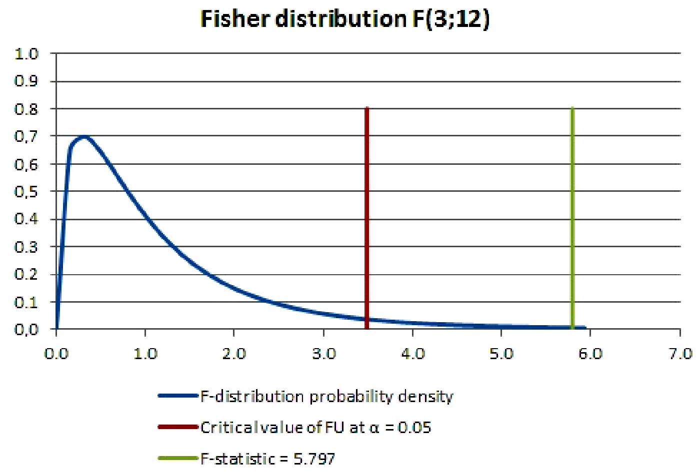


Figure 3: Fisher distribution for PEHS treatment temperature of 20 °C

Table 7
Results of one-factor analysis of variance for SPMS treatment condition

Time	Source of variance	Sum of squares	Number of degrees of freedom	Variance	Fisher's statistics, *F*	*P*-value	F_U
1 hour	Between groups	3.01445	2	1.507225	0.689131	0.52666	4.256495
	Within groups	19.68425	9	2.187139			
	Total	22.6987	11				
2 hours	Between groups	3.12635	2	1.563175	0.434767	0.660323	4.256495
	Within	32.35888	9	3.595431			

	groups						
	Total	35.48523	11				
3 hours	Between groups	3.225817	2	1.612908	0.394418	0.685175	4.256495
	Within groups	36.80408	9	4.089342			
	Total	40.02989	11				
4 hours	Between groups	3.20285	2	1.601425	0.390837	0.687435	4.256495
	Within groups	36.87678	9	4.097419			
	Total	40.07963	11				

To reject the null hypothesis, this value must not exceed the significance level α. Moreover, the *P*-value indicates that the probability of finding such a difference or a greater one between the mathematical expectations of the general population, provided that they are actually the same, is equal to the calculated P-value.

Based on the above, let us analyze the results. From Table 4, we can conclude that the *F*-statistic is much smaller than the calculated value, so the null hypothesis does not contradict the results of observations at a given level of significance α = 5%. From this, it follows that during cellulose SPMS modification, the silicon content in the substrate does not depend on time.

The data in Table 5 confirm that at a fixed processing temperature of 20 to 60 degrees, the TES processing conditions affect the silicon content in the pulp, as for all temperatures, the *F*-statistic was higher than F_U and the *P*-value did not exceed the level of significance α = 5%. The Fisher distribution graphs in Figure 2 clearly show that the calculated *F*-statistic is greater than the upper critical value of F_U, and the null hypothesis H_0 is rejected.

According to the data in Table 6, at 20°, the *F*-statistic was higher than the F_U, and the probability that the *F*-statistic is not less than the calculated value under the true null hypothesis is 1%, so at 20°, we conclude that the processing conditions of PEHS affect the silicon content of cellulose. The Fisher distribution graph, which clearly illustrates the deviation of the H_0 hypothesis, is shown in Figure 3.

The *F*-statistics F_U were obtained at 40 and 60 degrees, indicating that the PEHS processing conditions no longer have a significant effect on the silicon content of the cellulose.

To determine the dependences of silicon content in % on OSC processing conditions at a fixed time, in each of the groups for one condition of OSC treatment, we take 4 values of silicon content in % (Table 1). The results of the calculations performed by the methods of one-factor analysis of variance for each type of OSC treatment condition are recorded in Tables 7-9.

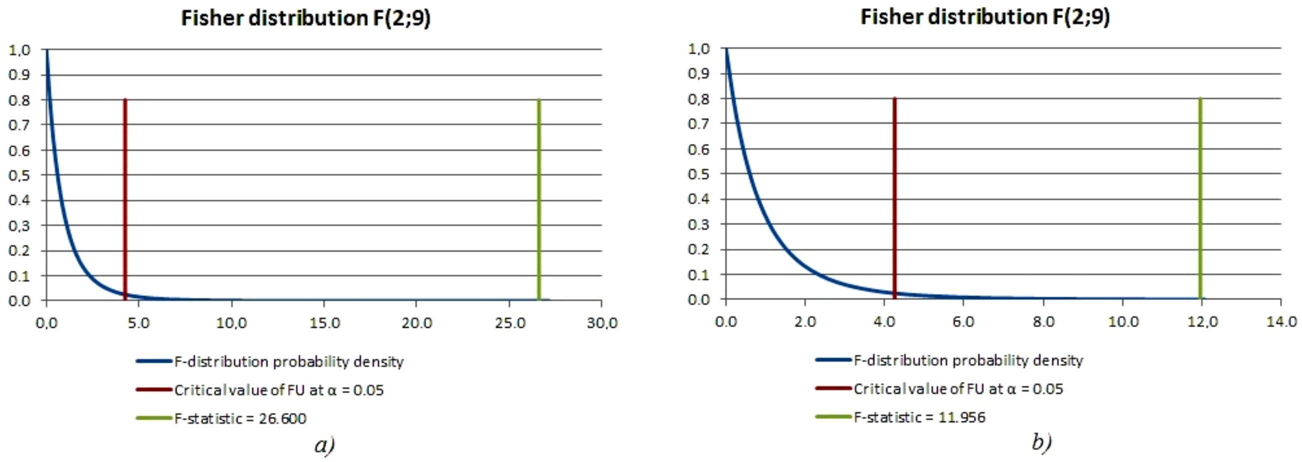
From Table 7, we can conclude that the *F*-statistic is much smaller than the calculated value, and hence the null hypothesis does not contradict the results of observations at a given level of significance α = 5%. From this, it follows that the treatment condition of SPMS has no significant effect on the silicon content of cellulose as a function of temperature.

The data in Table 8 confirm that at a fixed modification time of 1 hour and 2 hours, the conditions of TES processing affect the silicon content in cellulose, as the *F*-statistic was higher than F_U and the *P*-value did not exceed the significance level α = 5%. The Fisher distribution plots in Figure 4 show that the calculated F-statistic is much larger than the upper critical value of F_U, and the null hypothesis H_0 is rejected. However, for modification times of 3 and 4 hours, the analysis revealed that the *F*-statistics < F_U, *i.e.*, that the TES treatment conditions cease to have a significant effect on the silicon content of the pulp.

From the data in Table 9, we can see that at fixed modification times of 1, 2, 3, and 4 hours, the *F*-statistics > F_U, and the probability that under the true null hypothesis the *F*-statistics are not less than the calculated value varies from 0.4% to 4.2% and does not exceed the significance level α = 5%, so we can conclude that the PEHS processing conditions have a significant effect on the silicon content in cellulose at 20 to 60 degrees. Plots of the Fisher distribution are shown in Figure 5.

Table 8
Results of one-factor analysis of variance for TES treatment condition

Time	Source of variance	Sum of squares	Nr degrees of freedom	Variance	Fisher's statistics, F	P-value	F_U
1 hour	Between groups	0.204817	2	0.102408	26.59957	0.000167	4.256495
	Within groups	0.03465	9	0.00385			
	Total	0.239467	11				
2 hours	Between groups	0.2184	2	0.1092	11.9562	0.002924	4.256495
	Within groups	0.0822	9	0.009133			
	Total	0.3006	11				
3 hours	Between groups	0.245067	2	0.122533	3.757411	0.065112	4.256495
	Within groups	0.2935	9	0.032611			
	Total	0.538567	11				
4 hours	Between groups	0.248517	2	0.124258	3.422309	0.078455	4.256495
	Within groups	0.326775	9	0.036308			
	Total	0.575292	11				



a) b)

Figure 4: Fisher distribution for TES treatment conditions of time: (a) 1 h, (b) 2 h

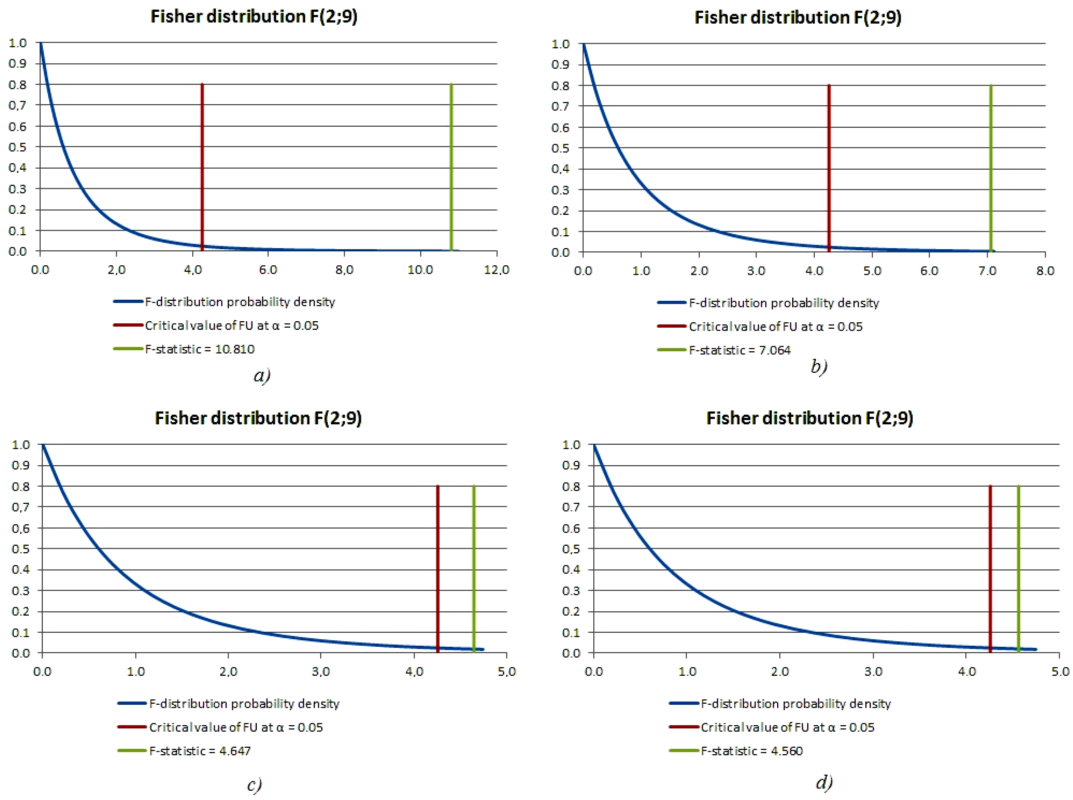
On the basis of the analysis, we can note the following. The pre-phosphorylation of the substrate increases the degree of its modification by the studied OSC. It is most likely due to the fact that polar OPC molecules, which have better penetrating and fixing abilities in the substrate, act as “conductors” of OPC into the substrate structure. It is possible that sequentially modifying cellulose with OPC and OSC results in OSC coordination to form an intermediate, including coordination of the =P: →Si = type, which facilitates the interaction of OSC functional groups with the OH-groups of cellulose. Increasing the soaking time and temperature also leads to an increase in the percentage of grafted silicon.

The influence of OPC of different nature on the degree of modification of the OSC substrate at different temperatures and modification times was established by methods of correlation analysis. It was found that there was a strong, direct correlation between the time of modification and the percentage of silicon content in the cellulose. The variation in the values of the calculated correlation coefficients ranged from 0.8927 to 0.9827. However, the direct correlation between the modification temperature and silicon content in cellulose in % was stronger, and the scatter of

correlation coefficients ranged from 0.9719 to 1.

Table 9
Results of one-factor analysis of variance for PEGS treatment condition

Time	Source of variance	Sum of squares	Nr degrees of freedom	Variance	Fisher's statistics, F	P-value	F_U
1 hour	Between groups	0.105817	2	0.052908	10.80988	0.004046541	4.256494729
	Within groups	0.04405	9	0.004894			
	Total	0.149867	11				
2 hours	Between groups	0.120317	2	0.060158	7.063601	0.014306632	4.256494729
	Within groups	0.07665	9	0.008517			
	Total	0.196967	11				
3 hours	Between groups	0.125267	2	0.062633	4.647156	0.041083645	4.256494729
	Within groups	0.1213	9	0.013478			
	Total	0.246567	11				
4 hours	Between groups	0.127717	2	0.063858	4.5595	0.042902958	4.256494729
	Within groups	0.12605	9	0.014006			
	Total	0.253767	11				



a) *b)* *c)* *d)*

Figure 5: Fisher distribution for PEHS treatment conditions of time (a) 1 h; (b) 2 h; (c) 3 h; (d) 4 h

Based on the correlation analysis performed, we can conclude that the most effective "conductor" of OSC into the substrate depending on modification time can be considered TCP at a modification temperature of 20 degrees because, under these conditions, the correlation coefficients of OSC are higher than for other conditions of OPC processing. DMP can be considered the most effective "conductor" of OSC into the substrate depending on the modification temperature because the correlation coefficients for all OSC are higher under these conditions than under other OPC processing conditions.

The effect of OSC treatment conditions on the silicon content of cellulose, expressed as a percentage of its weight, at different temperatures and modification times, was determined using the single-factor analysis of variance. The single-factor analysis of variance found that there was no relationship between the percentage of silicon in the substrate and the temperature and time of modification when the cellulose surface was modified with SPMS. We speculate that this may be due to the high reactivity of SPMS.

The analysis confirmed a significant effect of TES processing conditions on the silicon content of cellulose for 4 hours at fixed processing temperatures of 20, 40, and 60 degrees. The effect of TES treatment conditions at a fixed time on the silicon content in cellulose at 20 to 60 degrees was only found at a fixed time of 1 or 2 hours, as the *F*-statistic was much higher than the F_U and the *P*-value did not exceed the significance level of = 5%. For the modification times of 3 and 4 hours, the analysis revealed that the *F*-statistics < F_U, *i.e.*, that the TPP treatment conditions cease to have a significant effect on the silicon content of the pulp.

When using PEHS as a modifier, the analysis showed an effect on the silicon content from the processing time only at a temperature of 20 degrees. At 40 and 60 degrees, it was found that the PEHS treatment conditions no longer had a significant effect on the silicon content of the pulp. However, at fixed times of 1, 2, 3, and 4 hours, the analysis confirmed that the PEHS processing conditions had a significant effect on the silicon content of the cellulose at 20 to 60 degrees.

CONCLUSION

For each OSC, the most effective precursor for sequential modification in terms of the greatest silicon grafting into the substrate composition will be the following OPC. Depending on the time of modification:

- TCP will be the optimal precursor for SPMS at modification temperatures of 20 and 40 degrees, and TIT will be the optimal at temperatures of 60 degrees.
- TCP will be the optimal precursor for TES at modification temperatures of 20 degrees, and TIT will be the optimal at temperatures of 40 and 60 degrees.
- TCF would be the optimal precursor for PEHS at a modification temperature of 20 degrees, untreated OPC at 40 degrees, and DMP at 60 degrees.

Depending on the temperature of the modification:

- For SPMS, the optimal modification time is 1 hour; 2 or 4 hours; and 3 hours.
- DMP, TIT, and TCP would be optimal for TES with a 1 hour modification time; no OPC for 2 hours and 3 hours modification times; and DMP for 4 hours modification time.

The modification time of 1 hour for PEHS corresponds to DMP; the remaining modification times of 2, 3, and 4 hours correspond to TCP.

Thus, in this study, it was established for the first time that the most effective "conductor" of OSC to the substrate, depending on the time of modification, can be considered TCP at a modification temperature of 20 degrees. DMP at a modification time of 1 hour can be considered the most effective "conductor" of OSC into the substrate, depending on the modification temperature.

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