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RADIATION GRAFT COPOLYMERIZATION OF VINYL FLUORIDE TO COTTON, HYDROCELLULOSE FIBER AND FABRIC

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Cellulose-based materials are not in short supply and are characterized by relatively low cost. On the other hand, cellulose fibers have a wide range of valuable physical, chemical and mechanical properties that make them indispensable in a number of sectors of the national economy. Along with valuable qualities, natural and artificial cellulose fibers also have some disadvantages that limit their use in technology and in the national economy. These are low resistance to the action of microorganisms, relatively low heat resistance, chemical resistance, flammability, etc., which reduce their service life and limit their scope. One of the ways to eliminate these shortcomings is the modification of natural and artificial macromolecular compounds by chemical and physicochemical methods. Improving the properties of cellulose and its derivatives can be achieved by various modification methods, among which one of the most promising is the radiation-chemical grafting of various monomers. One of the advantages of this method, in comparison with others, is the production of field worlds that are not contaminated with impurities, the presence of which can adversely affect their physicochemical properties. Another advantage is the relative ease of formation of macroradicals necessary to initiate the process of graft copolymerization. Quite a lot of work has been devoted to the radiation grafting of various monomers to cellulose and its derivatives; at present, some of them are beginning to be widely used in the national economy. In the light of the foregoing, the grafting of fluorine-containing monomers, the polymers and copolmers of which have such very valuable and specific properties as high heat resistance, chemical resistance, light resistance, decay resistance and hydrophobicity to cellulose and its derivatives, is of great scientific and practical interest. This work is the synthesis of graft copolymers of cotton cellulose with vinyl fluoride by the radiation-chemical method from the vapor phase, the study of the effect of radiation dose rate, reaction time, the presence and nature of solvents on the course of this process and the yield of graft copolymers, as well as the study of such important physical and chemical properties and operational properties of the original, irradiated and grafted copolymers, such as sorption capacity and density, hydrophobicity and swelling, degree of whiteness, mechanical properties, thermal stability, the nature of the change in the supramolecular structure as a result of grafting fluorine-containing polymers.

Keywords: *Radiation grafting, Monomer; Thermal capacity; Thermal stability; Hydrophobicity; Degree of whiteness; Supramolecular structure; Fluorine-containing polymers*
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INTRODUCTION

One of the effective ways to modify the properties of cellulose fibers is their graft copolymerization with various vinyl monomirs. This leads to a significant improvement in such important physical, chemical and performance properties of cotton cellulose as sorption capacity, dyeability, resistance to the action of microorganisms, chemo- and heat resistance, etc [1, 3].

The schematic formation of cellulose graft copolymerization can be represented as follows:

$\text{Cell} \xrightarrow{\gamma} \text{Cell}^{O}. + \text{H}$ - formation of a free macroradical.

$\text{Cell}^{\,O} + \text{M} \longrightarrow \text{Cell} - \text{M}^{O}$ - initiation of the graft copolymerization reaction. where M is a monomer.

Chain termination occurs as a result of chain transfer to monomer or solvent molecules, as well as during the interaction of a growing chain with monomer radicals:

$\text{Cell}\,(\text{M})_{n-1} - \text{M}^{O} + \text{M} \longrightarrow \text{Cell} - (\text{M})_n + \text{M}^{O}$

$\text{Cell}(\text{M})_{n-1} - \text{M}^{O} + \text{R} \longrightarrow \text{Cell}(\text{M})_n + \text{R}^{0}$

$\text{Cell}(\text{M})_{n-2} - \text{M}^{O} + \text{M}^{O} \longrightarrow \text{Cell}(\text{M})_n$

This scheme is the most general, and in each specific case it is necessary to take into account the possibility of a particular process occurring.

One of the features of the grafting reaction to cellulose is the need to use various liquids or their vapors in order to swell cellulose in them. Cellulose swellings are more accessible to monomer molecules as a result of facilitating their diffusion inside the fibers [2].

As a result of numerous studies in the study of the process of graft copolymerization of a number of vinyl monomers to cellulose, it was found that in the presence of water, alcohols, amines and dimethylformamide, the yield of the graft copolymer increases, and in the presence of non-polar liquids such as benzene, toluene and others, the graft copolymerization reaction proceeds with very low efficiency [3].

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Japanese researchers have shown that for the synthesis of graft copolymers with a high yield by joint irradiation of cellulose and styrene, methyl methacrylate, or another vinyl monomer with Co^{60} γ-gamma rays, it is sufficient to use cellulose swollen in water. They also showed that in the absence of water or other solvents that cause swelling of cellulose, graft copolymerization practically does not occur [3-4].

The purpose of this work was to obtain new graft copolymers based on cotton cellulose with fluorine-containing monomers under laboratory conditions, to select methods and conditions for synthesis, as well as to comprehensively study some of the physicochemical and operational properties of the synthesized samples in order to determine and select their areas of application [5].

We took cellulose from cotton fiber and cotton fabric /coarse calico/ as initial samples. It can be noted that these preparations differ significantly from each other both in terms of the web of the molecular packaging and in other most important physicochemical properties. Cotton fiber always has various impurities such as hemicellulose, fats, wax, lignin, etc., which significantly affect its reactivity. Therefore, before use, cotton cellulose and cotton fabric were thoroughly cleaned of lubricants [6].

EXPERIMENTAL PART

Materials

For the synthesis of fluorine-containing graft copolymers, we used vinyl fluoride, ($CH_2 = CHF$) [7].

Sentiz vinyl fluoride was carried out by us by catalytic hydrofluorination of fine acetylene in the reaction:

$$CH \equiv CH + HF \frac{360 \div 380^{\circ}}{AlF_3 + C} = CH_2 = CHF$$

Industrial anhydrous hydrogen fluoride was used for the hydrofluorination of acetylene. Aluminum fluoride mixed with graphite was used as a catalyst. The resulting vinyl fluoride was purified by a chemical method to a high degree of purity, which was controlled using a gas chromatograph. Graft copolymers were synthesized by combined irradiation of cellulose fibers in vinyl fluoride vapor in the presence and absence of vapors of various solvents. The formation of the adopted copolymer was determined by weight gain and by analysis of the fluorine content in the adopted copolymer [7-9].

The polymer weight gain was calculated by the Equation:

$$A = \frac{A_1 + A_0}{A_1} \cdot 100$$

where A_0 is the weight of the initial polymer, A_1 is the weight of the graft copolymer [6-7].

The fluorine content in percent was calculated by the Equation:

$$x = \frac{0.000475(\upsilon_1 - \upsilon_2)}{g} K \cdot 100 = 0.0475 \frac{(\upsilon_1 - \upsilon_2)}{g} K$$

where υ_1 - is the volume of 0.025 N thorium nitrate solution used for titration of the test sample, *ml*. υ_2 - volume of 0.025 N thorium nitrate solution used for titration in a blank experiment, *ml*. 0.000475 - the amount of fluorine corresponding to 1 ml of 0.0025 N solution of thorium nitrate, *K*-correction factor for bringing the concentration of a solution of thorium nitrate *g*. *g*-sample weight, *g* [6-7].

The study of these polymers will make it possible to find the general patterns of grafting fluorine-containing monomers to cellulose and will lead to an improvement in some of their physicochemical performance properties. This will further expand the scope of their application in various sectors of the national economy, make them even more durable and valuable in operation [8]

We have studied the kinetics of grafting vinyl fluoride /VF/ to cotton cellulose, fabrics based on them. The results obtained show that the kinetics of grafting is influenced by various factors, such as dose, dose rate, presence of solvents, swelling of the starting and obtained materials in solvents, etc [9].

Sorption of water vapors was studied on a high-vacuum sorption setup such as McBain balances at 25°C\pm 0.2°C.

Determination of sorption is based on measuring the weight of a pre-dried sample in vacuum, as the water vapor pressure increases [15]. The dry sample weight was calculated using the Equation:

$$g_{dry} = g_{bl.} - \frac{r\Delta h}{1000} \tag{1}$$

where r is the sensitivity of the springs, *mg*/*mm*, Δh-difference of cathetometer readings before and after pumping out, *mm*, g_{dry} - weight of the sample after pumping out, *g* [10-13].

To determine the amount of moisture sorbed by the samples during each measurement of each sample, the constant *K* was calculated [10-13];

$$K = \frac{r}{g_{dry}} \cdot 100, \tag{2}$$

where *K* - shows the amount of sorbed water vapor as a percentage when the springs are extended by 1 *mm*.

The thermal stability of the samples was studied by the thermographic method on an instrument with Mac-Bon spring balances with a spiral sensitivity of *r*=1.96. The weight loss of the heated samples was recorded by the movement of a special mark in the field of the MG-1 horizontal microscope and was calculated in % according to the Eqs. [11-13].

$$K = \frac{r \cdot \Delta l}{g_l} \cdot 100\,,$$

where *P* is weight loss; Δl-difference of microscope readings; g_l- weight of dry sample, *g* [12]

RESULTS AND DISCUSSION

As experimental studies have shown, during the radiation-vapor-phase grafting of VF to the original cotton cellulose in the absence of vapors of various liquids, the yield of the grafted copolymer is negligible. For example, at a dose rate of 70 r/sec and an irradiation duration of 18 h, the PVF content in the graft copolymer is only 5.1%. As a result, in order to increase the yield of the graft copolymer and increase the efficiency, the graft copolymerization of VF and CC was carried out at a dose rate of 70 r/sec in the presence of vapors of various polar solvents that cause swelling of cellulose over a wide range of irradiation times [10-11].

The preliminary activation of the WF was also carried out by mercerization and incorporation of cellulose fibers.

Mercerization of cotton cellulose with 18% sodium hydroxide solution and inclusion with dimethylformamide /DMF/ and isoamyl alcohol was carried out according to the method indicated in the work [10].

The data obtained on the grafting of VF to various samples of cotton cellulose are shown in **Table 1**.

Table 1. Data on grafting vinyl fluoride to cotton cellulose at a dose rate of 70 r/s

Irradiation duration	The content of PVF in the copolymer, %	Grafting rate, %/hour	Irradiation duration, h	PVF content in copolymer, %	vaccination speed, %/hour
HC mercerized			**HC mercerized**		
2	1.0	0.5	2	1.5	0.45
4	1.3	0.33	4	1.85	0.45
6	2.3	0.38	6	2.9	0.48
10	2.7	0.27	8	4.5	0.56
14	3.7	0.26	12	5.9	0.49
16	4.4	0.28	14	7.0	0.51
18	5.1	0.28	16	8.2	0.51
20	5.7	0.29	18	9.0	0.50
HC, DMF included			**HC, saturated with DMF vapours**.		
4	3.7	0.92	4	4.9	1.22
6	4.6	0.76	6	6.1	1.16
10	6.0	0.6	8	8.2	1.25
12	6.9	0.57	10	9.0	0.90
14	7.8	0.55	12	9.7	0.80
16	8.2	0.51	16	11.4	0.71
18	9.4	0.50	18	10.7	0.59
HC inclued with isoamyl alcohol			**CHC, saturated with isoamyl alcohol vapors**		
3	5.6	1.86	4	7.1	1.77
5	7.0	1.40	6	8.2	1.36
7	9.1	1.30	8	9.6	1.20
14	12.0	0.85	16	12.6	0.80
18	11.9	0.66	18	13.8	0.70

As can be seen from the data presented in the table, in all cases, with an increase in the duration of irradiation, both the weight gain and the content of PVF increase, but there are, however, differences in the rate of grafting of VF to the original, mercerized, and included cellulose. At the same radiation dose rate, the grafting of VF to the original, mercerized and included cellulose proceeds at a significantly higher rate compared to untreated cotton cellulose. Such an increase in the rate of grafting after mercerized and incorporation is obviously associated with a significant loosening of the structure and with an increase in the reactivity of cotton cellulose during processing. This effect is especially noticeable in the case of incorporation of cellulose with isoamyl alcohol, while the maximum content of PVF in the graft copolymer reached 11.9%, while for the original cellulose it was 5.1%.

It has been experimentally established that during the grafting of fluorine-containing monomers to cellulose, it is most effective when it is carried out in the presence of vapors of polar solvents that cause swelling of cellulose. Based on this, the graft copolymerization of VF to cotton cellulose was carried out in the presence of vapors of the same inclusion solvents under identical conditions.

It should be noted that the grafting of VF to mercerized cellulose in the presence of DMF vapor and isoamyl alcohol proceeds more efficiently than to mercerized cellulose. This effect is due to the fact that in this case grafting occurs at the moment of swelling, which facilitates the diffusion of monomer vapor into the fiber.

In order to study the effect of different dose rates on the effectiveness of vaccination, it was carried out in the presence of methyl alcohol vapor at dose rates of 8.3; 44 and 90 r/sec. The results obtained are shown in **Table 2**.

Table 2. Data on grafting vinyl fluoride to cotton cellulose at different dose rates

Irradiation duration, h	Integral radiation dose, mr	PVF content in copolymer, %	Grafting rate, %/h
Dose rate 8.3 r/sec			
2	0.06	1.5	0.71
4	0.12	2.6	0.66
6	0.18	3.1	0.52
10	0.30	3.9	0.39
14	0.42	5.1	0.35
Dose rate 44 r/sec			
2	0.32	1.8	0.91
4	0.63	2.9	0.75
6	0.95	4.1	0.68
10	1.58	6.4	0.64
14	2.28	8.1	0.34
Dose rate 80 r/sec			
2	0.68	2.5	1.21
4	1.15	5.8	1.45
6	1.77	8.4	1.40
10	2.88	11.5	1.15
14	4.03	13.8	0.98

From the data obtained on the study of the effect of irradiation rate and dose on the yield of the graft copolymer (Table 2), it can be seen that with an increase in both the duration of irradiation and the dose rate, the yield of the graft copolymer increases.

Thus, based on the results obtained on the study of grafting of VF to CC, we found that the formation of a graft copolymer of cellulose with VF in the absence of liquids that cause swelling of cellulose is insignificant.

The most appropriate is the saturation of vapors and polar solvents of modified cellulose samples, which contributes to a significant increase in the amount of grafted PVF. For example, in the presence of DMF vapors in the duration of irradiation of 16 h, the content of PVF in the graft copolymer is 11.4%, while in its absence it is only 4.4%. Such an increase in the rate of grafting of HF to CC in the presence of DMF vapor is apparently due to the good swelling properties of cellulose in it, which facilitates the diffusion of HF molecules to polymer macroradicals [16].

In addition, a favorable effect on the grafting processes of DMF itself is not excluded, since it is a relatively radiation-sensitive substance and can play the role of chain transfer to the cellulose macromolecule.

Next, we studied the grafting of VF to cotton (cotton) fabric. Radiation vapor-phase grafted copolymerization of VF to cotton fabric was carried out both in the presence of methyl and ethyl alcohol vapors, and in their absence at a dose rate of 80 r/sec in a wide range of irradiation times. It has been experimentally shown that the grafting of HF to cotton fabric in the absence of vapors of polar solvents proceeds almost very little, just as in the case of grafting of HF to cotton fibers. Thus, for example, the maximum yield of the graft copolymer during 18 h of irradiation at a dose rate of 80 r/sec in the absence of solvent vapors reaches only 2.3%, while in the presence of methyl alcohol vapors under identical conditions, the yield reached up to 9.1% [10-20].

Obtaining the result of grafting VF to cotton fabric in the presence of vapors of methyl and ethyl alcohols and their absence are given in **Table 3**. As can be seen from the data presented, with an increase in the duration of irradiation, the content of PVF in the graft copolymer increases. When comparing the data obtained under the same conditions for the two solvents used, it was shown that they are close to each other in terms of grafting efficiency.

On the basis of the data obtained, it can be noted that as a result of grafting VF to CC fibers and cotton fabric grafting at a dose rate of 80 r/sec under the same synthesis conditions, the highest yield of the graft copolymer is observed when cotton fiber is used as a substrate. This result is apparently related to the structural difference between these two cellulose objects, as well as their chemical composition [13-18].

Thus, when studying the radiation-vapor-phase copolymerization of VF to CC fibers and cotton fabrics, it was found that the process and efficiency of grafting are significantly affected by various treatments of cellulose, the presence of vapors of various solvents, as well as the dose rate and duration of irradiation [16-20].

We have comprehensively studied such physicochemical properties of samples of graft copolymers, the initial polymer subjected to irradiation in vacuum and in the presence of vapors of various solvents, such as water vapor sorption and density, hydrophobicity, degree of whiteness, thermal and thermooxidative degradation.

Table 3. Data on the grafting of vinyl fluoride to cotton fabric in the absence and presence of solvent vapors at a dose rate of 80 r/sec

Irradiation duration, h	Integral radiation dose Mrad	The content of PVF in the copolymer, %	Grafting rate, %/hour
In a vacuum			
2	0.61	0.6	0.35
4	1.12	2.2	0.30
9	2.51	3.3	0.24
12	3.42	3.1	0.25
18	5.10	3.4	0.18
Cotton - fabric saturated with methyl alcohol vapors.			
3	0.83	1.7	0.58
6	1.76	2.7	0.46
9	2.51	4.9	0.54
12	3.46	6.6	0.55
15	4.32	8.6	0.56
18	5.10	9.8	0.54
Cotton - fabric saturated with ethyl alcohol vapors.			
2	**0.61**	**1.1**	**0.55**
4	**1.12**	**2.0**	**0.50**
9	**2.51**	**3.9**	**0.43**
12	**3.42**	**5.9**	**0.48**
18	**5.10**	**6.2**	**0.34**

The degree of whiteness of the obtained samples was determined on an FM-58 differential photometer and expressed as a percentage relative to the pain of a barite plate ($BaSO_4$), the whiteness of which is taken as 96%.

Sorption capacity was estimated by sorption isotherms obtained at 250C. Figure 1 shows the sorption isotherms of water vapor, mercerized cellulose and its graft copolymers, as well as the graft polymer PVF.

As can be seen from the figure, the change in the sorption isotherm of graft copolymers with increasing relative humidity also has an *S* - shaped character, and the values of water vapor sorption by graft copolymers are less than those of the original cellulose and, accordingly, decrease with an increase in the content of the graft polymer. PVF itself does not significantly absorb water vapor. For example, at 50% relative humidity, its value is only 0.2%, and a further increase in relative humidity almost does not lead to an increase in the sorption of this polymer. Based on this, we can say about the high hydrophobicity of PVF. Therefore, the study of the sorption capacity of cellulose preparations after their modification by grafting fluorine-containing polymers is of great theoretical and practical interest.

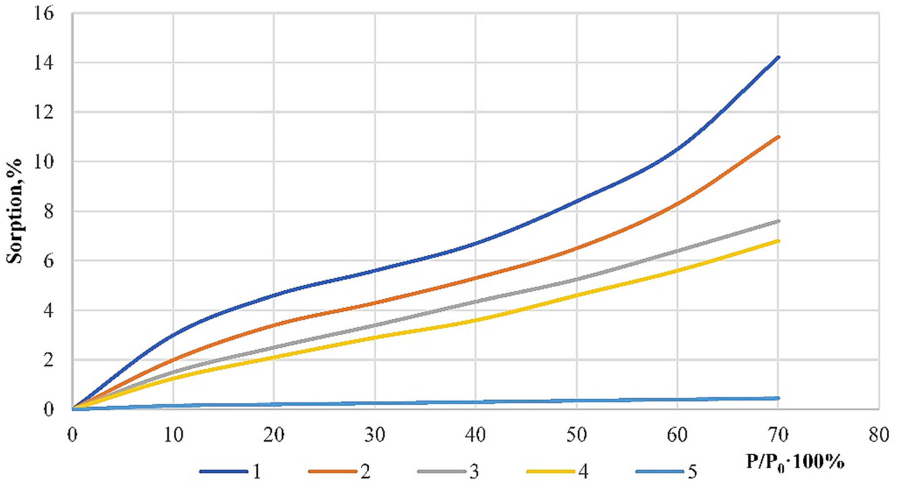

Figure 1. Water vapor sorption isotherms at 250C. 1 - mercerized CC, 2 - original CC, 3 - graft copolymers containing 4.5% PVF, 4 - graft copolymers containing 12.6% PVF, 5 - pure PVF.

Comparison of the sorption properties of the original, irradiated and grafted cellulose fibers and tissues was carried out at 50% relative humidity.

The obtained experimental data on the study of the sorption of water vapor and the density of the initial and irradiated, as well as graft copolymers of various types in cellulose are shown in **Table 4.** From the data in Table. it can be seen that after mercerization and incorporation of CC fibers, the sorption capacity increases significantly, and the density decreases accordingly. This effect is especially pronounced after the incorporation of CHC with isoamyl alcohol [1-5, 21-23].

Table 4. Results of changes in water vapor sorption and density of graft copolymers on cotton cellulose with different PVF content.

PVF content, %	**Sorption, %**	**Density, g/cm^3**		**Specific volume**	
				Calculated:	
		Found experimentally	**Calculated by additivity**	**experimental**	**by additivity**
Initial	6.3	1.5450	-	0.6472	-
1.3	5.1	1.5411	1.5420	0.6492	0.6484
3.7	4.8	1.5342	1.5384	0.6505	0.6503
5.8	5.0	1.5350	1.5366	0.6514	0.6507
HC-mercerized 18% - a OH					
0	8.2	1.5310	-	0.6531	-
2.9	7.7	1.5260	1.5271	0.6546	0.6541
5.9	7.7	1.5212	1.5228	0.6566	0.6567
9.0	68	1.5164	1.5185	0.6586	0.6584
CHC-included DMF					
0	8.5	1.5264	-	0.6550	-
3.7	8.3	1.5187	1.5248	0.6577	0.6558
6.9	7.0	1.5166	1.5192	0.6593	0.6580
7.8	6.7	1.5140	1.5159	0.6601	0.6590
HC-included with isoamyl alcohol					
0	9.0	1.4921	-	0.6687	-
5.6	7.6	1.4848	1.4860	0.6735	0.6722
7.0	7.0	1.4819	1.4820	0.6747	0.6734
9.1	-	1.4785	1.4829	0.6764	0.6743
12.0	5.6	1.4746	1.4799	0.6781	0.6756
HC-vapour-saturated DMF					
0	8.2	1.5310	-	0.6531	-
4.9	7.3	1.5230	1.5241	0.6566	0.6559
6.1	6.3	1.5190	1.5225	0.6582	0.6567
9.7	6.6	1.5161	1.5191	0.6587	0.6580
11.4	5	1.5152	1.5152	0.6605	0.6591

The data on the sorption capacity and density of the grafted copolymers show that grafting VF to fibers causes a noticeable decrease in their sorption capacity and density compared to the original sample. At the same time, with an increase in the content of PVF in them, these values gradually decrease, and the decrease in the sorption capacity is proportional to the content of grafted polymers in the modified samples (**Fig. 2**).

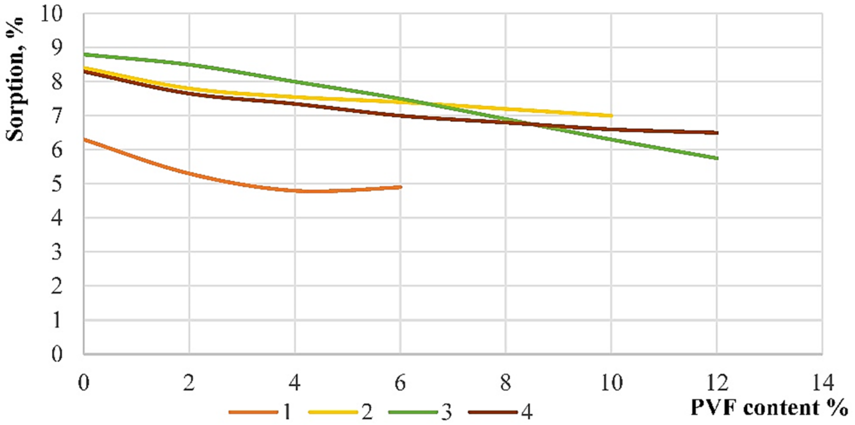

Figure 2. Dependence of the sorption capacity of CC-PVF graft copolymers on the content of PVF
1 - initial CC, 2 - mercerized CC, 3 - included CC with isoamyl alcohol, and 4 - DMF

This effect is obviously related to the significant supramolecular structure of cellulose in the act of grafting. During the grafting process, the monomer molecules diffuse into the pores and somewhat fill them due to the formation of a graft copolymer, which is more hydrophobic than the original cellulose, and therefore the sorption capacity of those modified by the sample decreases [3-8, 10-13].

In order to elucidate the influence of the duration of irradiation, the nature of the solvent, and the presence of grafted fluorine-containing chains on the change in the whiteness of cellulose samples, we studied the degree of whiteness of the original cotton fabric samples irradiated in vacuum and in methyl alcohol vapor, as well as their grafted copolymers with VF. The results of the study are shown in **Table 5**.

Table 5. The result of changing the degree of whiteness of irradiated and grafted copolymers of cotton fabric with PVF

Integral dose of radiation, mr	Degree of whiteness of tissue irradiation, %		Graft copolymers	
	in a vacuum	In the environment of vapors of methyl alcohol	PVF content, %	Degree of whiteness, %
original sample	79.0			
1.00	78.0	78.0	3.3	88.4
1.67	76.1	79.3	4.8	88.9
2.33	72.2	84.3	9.1	83.5
3.34	70.9	86.0	12.3	94.5
5.01	70.1	83.9	14.9	95.3
6.01	68.5	86.2	16.1	96.6

As can be seen from the data obtained, **Table 5**. With an increase in the integral dose of irradiation, the degree of whiteness of irradiated cotton fabrics decreases significantly, and the greater the effect of the radiation dose, the less the decrease in the degree of whiteness. However, as a result of irradiation of cotton fibers and fabrics in an environment of methyl alcohol vapor, on the contrary, with an increase in the duration of irradiation, the degree of whiteness of the irradiated samples increases significantly, while during their irradiation in an environment of isoamyl alcohol and in dimethylformamide this effect also deteriorates, as well as in the case of irradiation in vacuum. Modified samples of viscose cellulose by PVF grafting, obtained in an environment of vapors of methyl and ethyl alcohols, are distinguished by their high whiteness. For example, when irradiated with 5.1 mr, cotton fabric loses its whiteness from 79% to 70.1% under the same conditions, an irradiated fabric containing 14.9% PVF has a whiteness of 96.3%. As can be seen from the table, the greater the content of the grafted polymer in the copolymer, the greater the increase in the degree of whiteness of the modified cotton fabrics. Such an increase in the whiteness of cotton as a result of grafting and irradiation in an environment of methanol vapor is apparently due to the fact that the grafted PVF polymers have a higher whiteness than hydrated cellulose.

Thermogravimetric experiments were carried out in the temperature range from 230°C to 255°C in vacuum and at 230°C in air. The original and modified with cotton fibers and fabrics containing 10.6-16.4% of grafted PVF, as well as irradiated in vacuum in the irradiation time interval of 10-30 h at a dose rate of 90 r/sec, were subjected to the study.

The results obtained are shown in **Fig. 3.** When cotton is irradiated both in vacuum and in the presence of methyl alcohol vapor, its weight loss increases somewhat.

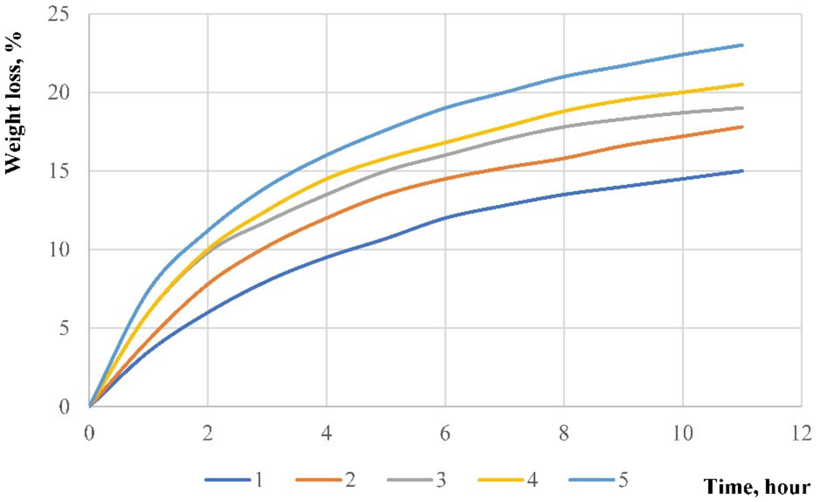

Figure 3. Kinetics of thermal degradation of the original irradiated and grafted copolymers of cotton fabrics with PVF in vacuum at 245°C. 1 – original cotton, 2 – irradiated cotton, 3 – irradiated in methanol vapor, 4,5 – grafting copolymer containing 12 and 16% PVF, respectively

The decrease in the thermal stability of irradiated samples is proportional to the duration of irradiation. The longer the duration of irradiation, the less the decrease in their thermal stability. This effect is explained by destructive processes leading to the formation of labile points in relation to the effects of elevated temperatures [18-22].

It can be seen from the obtained data that, in contrast to the initial and irradiated samples, the graft copolymers of C/b with PVF are characterized by higher thermal stability. For example, graft copolymers of C-fabric containing 12 to 16.4% when heated for 10 h at 245°C in vacuum lose 15.8 and 12.8%, respectively, while the original cotton fabric loses weight 20.9%.

When mixed under certain technological conditions and at a certain temperature, and also, in principle, from different polyelectrolytes with different structures, a new, individual substance was obtained, which differed both in properties and in structure from the original components shown in **Fig. 3**.

CONCLUSIONS

In order to improve some of the most important physicochemical and operational properties, radiation grafting of vinyl fluoride from the vapor phase to cotton cellulose and fabrics based on them was carried out [18-23].

The influence of power, radiation dose, presence and nature of solvents on the kinetics of grafting and the yield of graft copolymers has been studied. It has been found that with increasing dose rate, the grafting rate and the yield of the grafted copolymer increase, while the radiation-chemical yield decreases. The grafting rate of the selected monomer is proportional to the dose rate to the power of 0.5-0.6 [21-23].

It has been established that with an increase in the content of grafted fluorine-containing chains, the sorption capacity and swelling capacity of cellulose samples in water decreases, which is due to the hydrophobicity of the modifying polymers.

It has been shown that graft copolymers of cellulose with fluorine-containing polymers are characterized by increased thermal stability. At the same time, as the content of graft polymers increases, the temperature of the onset of decomposition increases, and the amount of weight loss decreases.

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REFERENCES

[1] Kang, Hongliang; Liu, Ruigang; Huang, Yong, "Graft modification of cellulose: Methods, properties and applications," Polymer, **70**, A1–A16 (2015). https://doi.org/10.1016/j.polymer.2015.05.041

[2] R. Keldibekova, S. Suleimenova, G. Nurgozhina, and E. Kopishev, "Interpolymer Complexes Based on Cellulose Ethers: Application," Polymers, **15**, 3326 (2023). https://doi.org/10.3390/polym15153326

[3] A.K. Bajpai, and J. Shrivastava, "Amylase induced enhanced enzymatic degradation of binary grafted polymeric blends of crosslinked starch and gelatin," J. Macromol. Sci. Part A: Pure Appl. Chem. **41**, 949–69 (2004). https://doi.org/10.1081/MA-120039181

[4] S.Ya. Inagamov, and G.I. Mukhamedov, "Structure and physical–mechanical properties of interpolymeric complexes based on sodium carboxymethylcellulose," Journal of Applied Polymer Science, **122**(3), 1749-1757 (2011). https://doi.org/10.1002/app.34222

[5] CH.R. Jagadish, A. Ferri, S. Giraud, J. Guan, and S. Fabien, "Chitosan–Carboxymethylcellulose-Based Polyelectrolyte Complexation and Microcapsule Shell Formulation," Int. J. Mol. Sci. **19**, 2521 (2018). https://doi.org/10.3390/ijms19092521

[6] M.A. Barakat, El-Salmawy, and A.H. Zahran, "Radiation Induced Grafting of Viscose Rayon Fabrics with Some Acrylic Acid Derivatives and Styrene," Open Journal of Polymer Chemistry, **7**, 1-18 (2017). https://doi.org/10.4236/ojpchem.2017.71001

[7] A. Vega-Paz, F. de J. Guevara-Rodriguez, J.F. Palomeque-Santiago, N.V. Likhanova, "Polymer weight determination from numerical and experimental data of the reduced viscosity of polymer in brine," Rev. Mex. Fís. **65**(4), 321–327 (2019). https://doi.org/10.31349/revmexfis.65.321

[8] J.S. Forsythe, and D.J.T. Hill, "The radiation chemistry of fluoropolymers," Prog. Polym. Sci. **25**, 101-136 (2000). https://doi.org/10.1016/S0079-6700(00)00008-3

[9] Z.A. Kenessova, G.A. Mun, B. Bakytzhanuly, R.K. Rakhmetullayeva, A.N. Yessirkepova, N.O. Samenova, and P.I. Urkimbayeva, "Radiation-Chemical Synthesis of Crosslinked Films Based on N-Vinylcaprolactam Copolymers," Bull. Exp. Biol. Med. **167**, 685–688 (2019). https://doi.org/10.1007/s10517-019-04599-6

[10] M.M. Ghobashy, "Ionizing Radiation-Induced Polymerization," in: *Ionizing Radiation Effects and Applications*, edited by B. Djezzar, (InTech, 2018). https://doi.org/10.5772/intechopen.73234

[11] K. Saito, K. Fujiwara, and T. Sugo, "Fundamentals of Radiation-Incduced graft Polymerization," in: *Innovative Polymeric Adsorbents*, (Springer, Singapore, 2018). pp. 1–22. http://dx.doi.org/10.1007/978-981-10-8563-5_1

[12] K. Saito, and T. Sugo, "High-performance polymeric materials for separation and reaction, prepared by radiation-induced graft polymerization," in: *Radiation Chemistry: Present Status and Future Trends*, edited by C.D. Jonah, and M. Rao, 1st ed., Vol. 87, (Elsevier, 2001), pp. 671–704.

[13] M.M. Nasef, and O. Güven, "Radiation-grafted copolymers for separation and purification purpose: Status, challenges and future directions," Progress in Polymer Science, **37**(12), 1597-1656 (2012). https://doi.org/10.1016/j.progpolymsci.2012.07.004

[14] N.A. Zubair, M.M. Nasef, T.M.Ting, E.C. Abdullah, and A. Ahmad, "Radiation induced graft copolymerization of amine-containing monomer onto polyethylene coated propylene for CO_2 adsorption," IOP Conf. Ser.: Mater. Sci. Eng. **808**, 012028 (2020). https://doi.org/10.1088/1757-899X/808/1/012028

[15] B. Singh, and A. Kumar, "Radiation-induced graft copolymerization of N-vinyl imidazole onto moringa gum polysaccharide for making hydrogels for biomedical applications," International Journal of Biological Macromolecules, Part B, **120**, 1369-1378 (2018). https://doi.org/10.1016/j.ijbiomac.2018.09.148

[16] S.Ya. Inagamov, U.A. Asrorov, N.T. Qodirova, O.T. Yomgirov, and G.I. Mukhamedov, "Development of Interpolymer Complexes Based on Sodium Carboxymethylcellulose and Polyacrylamide," in: *II International Scientific and Practical Conference "Technologies, Materials Science and Engineering, AIP Conf. Proc.* **2999**, 020049 (2023). https://doi.org/10.1063/5.0158621

[17] S.Ya. Inagamov, U.A. Asrorov, and E.B. Xujanov, "Structure and physico-mechanical properties of polyelectrolyte complexes based on sodium carboxymethylcellulose polysaccharide and polyacrylamide," East European Journal of Physics, 4, 258-266 (2023). https://doi.org/10.26565/2312-4334-2023-4-32

[18] T.T. Muratov, The Effect of Stabilizing the Lifetime of Charge Carriers in Semiconductors in a Magnetic Field, Moscow University Physics Bulletin, **78**(2), 199–203 (2023). https://doi.org/10.3103/S002713492302008X

[19] J.M. Khakkulov, A.A. Kholmuminov, and Z.S. Temirov, “Features of electrochemical reduction of silk fibroin in the presence of phosphate tricalcium in the form of nanocating,” Modern Physics Letters B, **5**(31), 2150476 (2021). https://doi.org/10.1142/S0217984921504765
[20] A.A. Kossov, Ph.D. thesis, A.V. Topchiev Institute of Petroleum Chemistry synthesis, Moscov, 2014. (in Russian)
[21] E.E. Shchadilova, Ph.D. thesis, St. Petersburg State Technological Institute. St. Petersburg, 2013. (in Russian)
[22] A.N. Mudrov, Ph.D. thesis, Ivanovo State chemical technology University of Ivanovo, 2013. (in Russian)
[23] V.F. Danilov, Ph.D. thesis, Kazan National Research Technological University, Kazan, 2013. (in Russian)

РАДІАЦІЙНА КОПОЛІМЕРИЗАЦІЯ ВІНІЛФТОРИДУ ДО БАВОВНИ, ГІДРОЦЕЛЮЛОЗНОГО ВОЛОКНА ТА ТКАНИН

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Матеріали на основі целюлози не є дефіцитом і характеризуються відносно невисокою вартістю. З іншого боку, целюлозні волокна мають широкий спектр цінних фізико-хімічних і механічних властивостей, що робить їх незамінними в ряді галузей народного господарства. Натуральні та штучні целюлозні волокна поряд з цінними якостями мають і недоліки, що обмежують їх використання в техніці та народному господарстві. Це низька стійкість до дії мікроорганізмів, відносно низька термостійкість, хімічна стійкість, горючість тощо, що зменшує термін їх служби та обмежує сферу застосування. Одним із шляхів усунення цих недоліків є модифікація природних і штучних високомолекулярних сполук хімічними і фізико-хімічними методами. Поліпшення властивостей целюлози та її похідних можна досягти різними методами модифікації, серед яких одним із найперспективніших є радіаційно-хімічне щеплення різноманітних мономерів. Однією з переваг цього методу в порівнянні з іншими є отримання польових світів, не забруднених домішками, присутність яких може негативно вплинути на їх фізико-хімічні властивості. Іншою перевагою є відносна легкість утворення макрорадикалів, необхідних для ініціювання процесу прищепленої кополімеризації. Досить багато робіт присвячено радіаційному прищепленню різних мономерів до целюлози та її похідних; в даний час деякі з них починають широко використовуватися в народному господарстві. У світлі вищевикладеного щеплення фторовмісних мономерів, полімери та кополімери яких мають такі дуже цінні та специфічні властивості, як висока термостійкість, хімічна стійкість, світлостійкість, стійкість до гниття та гідрофобність до целюлози та її похідних, представляє великий науковий і практичний інтерес. Дана робота полягає в синтезі графт-кополімерів бавовняної целюлози з вінілфторидом радіаційно-хімічним методом з парової фази, дослідженні впливу потужності дози опромінення, часу реакції, наявності та природи розчинників на перебіг цього процесу. і виходу прищеплених кополімерів, а також дослідження таких важливих фізико-хімічних властивостей і експлуатаційних властивостей вихідних, опромінених і щеплених кополімерів, як сорбційна ємність і щільність, гідрофобність і набухання, ступінь білизни, механічні властивості, термічні стабільність, характер зміни надмолекулярної структури в результаті щеплення фторовмісних полімерів.

Ключові слова: *радіаційне щеплення, мономер; теплова потужність; термостабільність; гідрофобність; ступінь білизни; супрамолекулярна структура; фторовмісні полімери*