

# Radiation Grafted Copolymerization of Vinylidene Fluoride to Cotton Cellulose and Hydrated Cellulose Fibers

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**Abstract:** Modifying cellulose hydrate using chemical and physicochemical techniques is one option to get rid of its drawbacks. Radiation-chemical grafting of different monomers is one of the most promising modification techniques [1] for improving the characteristics of hydrated cellulose and its derivatives. Radiation grafting of various monomers to hydrated cellulose (H/c) and its derivatives has been the subject of numerous studies [2], and some of these are now starting to find widespread application in the economy. Given the aforementioned, grafting fluorine-containing monomers onto hydrated cellulose and its derivatives – whose polymers and copolymers have highly valuable and specific properties like chemical resistance, high thermal stability, decay resistance, and hydrophobicity – represents a significant scientific and practical interest [3]. This work aims to synthesise grafted copolymers of hydrated cellulose with vinylidene fluoride from the vapour phase using a radiation-chemical method. The effects of radiation dose intensity, exposure duration, and solvent type on the process and grafted copolymer yield are investigated. Important physicochemical and functional characteristics of the original, irradiated and grafted copolymers are also examined in this study. These characteristics include sorption capacity, density, hydrophobicity, degree of whiteness, mechanical properties, thermal stability, and the type of supramolecular structure alterations brought about by grafting fluorine-containing polymers.

## 1 INTRODUCTION

Graft copolymerisation with vinylidene fluoride is one efficient method of changing the characteristics of hydrated cellulose fibre textiles. Important physicochemical and functional characteristics of hydrated cellulose, such as sorption capacity, whiteness degree, resistance to microbes, chemical and thermal capacity, and others, are significantly improved as a result. Numerous investigations into the graft copolymerisation process of various vinyl monomers to cellulose have revealed that the yield of the graft copolymer rises when water, alcohols, amines, and dimethyl formamide are present [4]. However, the graft copolymerisation reaction continues with relatively poor efficiency when nonpolar liquids like benzene, toluene, and others are present. Japanese researchers have demonstrated [5] that cellulose swelled in water is adequate for the manufacture of high-yield graft copolymers when

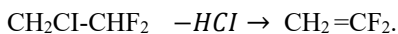
cellulose is irradiated with methyl methacrylate, styrene, or another vinyl monomer using  $\gamma$ -rays from  $Co^{60}$ .

The objective of this work was to create new copolymers with grafts that combined cotton and hydrated cellulose with a fluorine-based monomer in a lab setting, choose synthesis techniques, and thoroughly examine some physicochemical and operational characteristics of the synthesised samples to identify potential applications.

## 2 EXPERIMENTAL PART

Cotton cellulose and moistened cellulose fibres served as our first samples. It is noteworthy that the density, molecular packing, and other crucial physicochemical characteristics of these samples vary greatly from one another. The reactivity of cotton and hydrated cellulose fibres is greatly

impacted by a variety of contaminants, including hemicellulose, lipids, wax, lignin, and others. As a result, the samples were completely lubricant-free before being used. We created the monomer vinylidene fluoride (VF<sub>2</sub>) by pyrolysing monochlorovanilidene at temperatures between 680 and 700°C;  $-CH_2Cl - CHF_2$ ;



Gas chromatography was used to assess the resulting monomer [6] after it had been chemically purified to an exceptionally high level of purity. The presence of two fluorine atoms in the molecule (VF<sub>2</sub>) results in the polymer of this monomer exhibiting more pronounced specific properties compared to polyvinyl fluoride. For example, it is more resistant

to the action of microorganisms, thermo-oxidative effects, possesses high strength, atmospheric stability, and low water absorption [7]. Therefore, grafting this monomer onto natural fibers represents both theoretical and practical interest. In addition, it should be noted that there is no literature available on the grafting of VF<sub>2</sub> to C/F [8]. Our studies on the radiation polymerization of VF<sub>2</sub> and its grafting onto cellulose fibers showed that it has greater polymerization activity than grafting, compared to vinyl fluoride. Based on this, radiation graft copolymerisation was performed in the presence of vapours of different solvents with an integrated irradiation dosage of 2.5 M rad and a dose rate of 70 rad/sec in order to speed up the grafting rate of C/F and boost the yield of the grafted copolymer.

The obtained results are presented in Table 1.

Table 1: Effect of vapors of various solvents on the grafting degree of vinylidene fluoride onto cotton cellulose.

Solvent	Weight Added %	Content Of PVF <sub>2</sub> , %	Solvent	Weight Added %	Content Of PVF <sub>2</sub> , %
Absence Of	0,0	1,2	Isoamyl Alcohol	6,3	7,4
Water	4,1	5,0	Amyl Alcohol	3,1	5,4
Methyl Alcohol	6,7	8,1	Diethylamine	3,1	4,5
Ethyl Alcohol	5,8	7,2	Benchmark: Water 1: 25	5,2	6,8
Propyl Alcohol	4,5	6,6	Acetic Acid	4,1	5,8
Isopropyl Alcohol	6,8	7,1	Dimethylformamide (DMFA)	8,1	11,0

Table 2: Data on the grafting of vinylidene fluoride onto cotton cellulose at different dose rates.

Duration of irradiation	Integral dose of irradiation (M.R.)	Content of PVF <sub>2</sub> , %	Inoculation rate % per hour	Radiochemical yield of 10-3 mol/100 eV
Dose rate 11 r/s				
2	0,08	1,5	0,75	5,04
4	0,16	2,1	0,52	3,84
6	0,24	2,9	0,48	3,67
9	0,35	3,4	0,38	2,94
12	0,47	3,7	0,31	2,36
15	0,59	4,2	0,28	2,32
Dose rate 60 r/s				
2	0,43	2,1	1,00	1,45
4	0,86	3,2	0,80	1,12
6	1,30	4,4	0,73	1,03
9	2,04	5,6	0,62	0,86
12	2,59	6,0	0,50	0,66
15	3,24	6,4	0,43	0,63
Dose rate 90 r/s				
2	0,65	2,2	1,10	1,01
4	1,30	4,0	1,02	0,97
6	1,94	5,3	0,90	0,83
8	2,90	5,5	0,61	0,54
11	3,56	7,0	0,63	0,60
15	4,86	8,0	0,53	0,52

Table 3: The radiation vapor-phase graft copolymerization of vinylidene fluoride onto H/C was carried out in the presence of vapors of certain solvents with an integral irradiation dose of 2.5 Mrad and a dose rate of 70 rad/sec.

Duration of irradiation	Weight gain%	Content of PVF <sub>2</sub> in copolymer, %	Weight gain%	Content of PVF <sub>2</sub> in copolymer, %
In the vacuum			In the presence of water vapour	
3,0	0,4	0,4	2,0	2,0
5,5	1,0	1,0	2,2	2,1
7,5	1,1	1,1	3,7	3,9
10,0	1,1	2,2	4,4	4,8
13,0	1,6	2,4	5,1	5,3
17,0	1,5	2,3	5,7	6,1
In the presence of methyl alcohol vapors			In the presence of ethyl alcohol vapors	
3,0	2,2	3,2	2,6	2,3
5,5	3,1	5,0	3,0	4,2
8,0	5,4	5,5	3,8	4,5
11,0	6,9	7,08	4,0	4,6
16,0	8,5	8,7	5,1	5,6
17,0	9,0	9,1	6,2	6,6
In the presence of DMFA vapors				
3,0	2,0	2,55		
5,0	3,51	3,52		
8,0	4,8	4,8		
10,0	6,9	7,3		
13,0	10,1	11,5		
17,0	10,3	11,5		

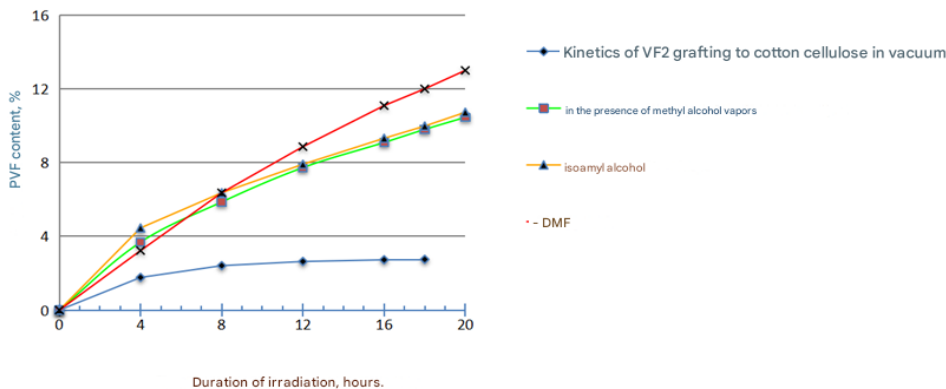


Figure 1: Grafting to cotton fiber.

As seen from Table 1, under the same conditions, the vapors of various solvents have a different effect on the formation of the grafted copolymer. A high graft yield is observed in the presence of a solution of DMF, methyl, isoamyl and ethyl alcohols. Therefore, in studying the kinetic patterns of the graft copolymerization of VF<sub>2</sub> onto C/F in the presence of alcohols, we chose these liquids as solvents. The results of the study on the grafting kinetics are shown in Figure 1, where the graphical dependence of the content of PVDF (poly vinylidene fluoride) in percentage on the irradiation duration is presented. As seen from the data obtained, when grafting was

carried out in the presence of solvent vapors, both the grafting yield and the content of poly vinylidene fluoride significantly increased with the irradiation duration.

Under the same conditions, the highest yield of the grafted copolymer is observed in the presence of DMFA vapors. The maximum content of PVDF in the copolymer is 12.8%. In order to study the effect of dose rate on the grafting efficiency, the grafting of VF<sub>2</sub> onto C/F was carried out at dose rates of 11, 60, and 90 rad/sec, within an irradiation time range of 2 to 15 hours, with an initial polymer-to-monomer ratio of 1:2. Table 2.

As seen from the presented Table, at all dose rates, the content of PVDF in the grafted copolymer increases with the irradiation duration. The experiment showed that in the absence of a solvent, VF<sub>2</sub> is also difficult to graft onto cotton cellulose; in this case, the grafted copolymer after 19 hours of irradiation at a dose rate of 80 rad/s in the absence of solvent vapors, the yield is 2.2%, and in the presence of methyl alcohol vapors under the same conditions, the yield is 8.1%.

Table 4: Data on the grafting of vinylidene fluoride to cellulose hydrate fiber in the absence and presence of vapors of various solvents (dose rate 70 rad/sec).

Solvent	Weight gain, %	Content of PVF <sub>2</sub> in the copolymer
-	1,0	2,2
Water	3,0	3,5
Methanol	4,1	6,2
Ethanol	2,9	3,2
Propanol	1,8	2,5
Isopropanol	1,9	2,5
Amyl Alcohol	2,8	3,2
Isoamyl Alcohol	2,4	5,3
Diethylamine	3,1	3,4
Dimethylformamide	6,2	7,0

The grafting of vinylidene fluoride to G/c was carried out in the presence of solvents at an integral

irradiation dose of 2.5 Mrad and a dose rate of 70 rad/s. The obtained data are presented in Table 3.

As seen from the Table 3, under the same conditions, the vapors of the solvents used have a different effect on the formation of the grafted copolymer. The most favorable effect on the grafting process is exerted by dimethylformamide, isoamyl alcohol, and methyl alcohol vapors. In this case, the yield of the grafted copolymer is significantly higher than in the presence of vapors of other solvents. Next, we studied the kinetics of VF<sub>2</sub> grafting onto H/C in the absence and presence of the vapors of the aforementioned solvents at a dose rate of 70 rad/sec over a wide irradiation time range. The obtained results are presented in Table 4. As seen from the data, grafting of VF<sub>2</sub> in the absence of solvent vapors occurs very insignificantly. For example, the maximum content of PVDF after 17 hours of irradiation reached only 2.5%, whereas under the same conditions, in the presence of water vapor, it reached 6.1%, in the presence of methyl alcohol vapors – 9.1%, and in the presence of dimethyl formamide vapors – 11.5%. As a rule, the behavior of the grafting process in the presence of vapors of solvents that cause polymer substrate swelling always leads to an increase in the grafting rate. This pattern was also observed in our case of grafting VF<sub>2</sub> onto hydrated cellulose fabric.

Table 5: Results of grafting vinylidene fluoride onto cellulose hydrate fibers at different dose rates

Irradiation duration, hours	Integral radiation doses, Mr	Content of PVF <sub>2</sub> in the copolymer, %	Inoculation rate, %/hour	Radiochemical yield 10 <sup>3</sup> mol/100 eq.
Dose rate 11 r/s				
3	0,12	1,4	0,47	3,42
5	0,20	1,9	0,39	2,81
8	0,32	2,2	0,27	2,00
11	0,44	2,7	0,24	1,83
17	0,73	3,4	0,20	1,27
20	0,89	3,3	0,16	1,20
Dose rate 68 r/s				
3	0,75	3,1	1,03	1,25
5	1,22	5,1	1,01	1,31
8	1,69	5,5	0,68	0,87
11	2,69	7,1	0,64	0,83
13	3,18	8,4	0,64	0,81
17	4,16	9,1	0,53	0,78
Dose rate 100 r/s				
2	0,90	4,2	1,68	1,30
5	1,80	5,7	1,14	0,98
7	2,60	6,4	0,85	0,89
10	3,60	6,3	0,62	0,53
13	4,68	8,5	0,66	0,51
17	6,10	8,9	0,52	0,42
20	7,20	9,1	0,45	0,40

Table 6: The changes in the degree of whiteness of irradiated and grafted H/C fabric samples with VF<sub>2</sub> are shown.

Integral radiation dose, Mr	Degree of whiteness of tissue irradiation%		Grafted copolymers	
	in vacuum	in the vapor of methanol	Content of PVF <sub>2</sub> %	degree of whiteness,%
Initial	79,0			
1,00	78,0	78,0	1,1	79,0
1,67	76,1	79,3	2,8	84,3
2,33	72,2	84,3	3,1	85,0
3,34	70,9	86,0	4,5	91,0
5,01	70,1	83,9	5,2	89,1
6,01	68,5	86,2	9,2	89,1

Table 7: Results of the change in water vapor sorption of grafted copolymers of C/F and H/C with different PVDF content.

Obtained in vacuum			Obtained in the vapour of methanol		
Grafted copolymers of hc fibers					
Starting Materials	0	6,3	0	0,0	6,3
2	0,7	6,0	2	2,6	5,2
4	1,9	5,4	4	4,7	4,4
6	2,1	5,2	9	6,8	4,1
12	2,8	5,0	12	8,0	4,0
15	2,9	4,9	15	9,2	4,3
Grafted Copolymers of G/C Fibers					
Starting Materials	0	11,4	0	0	11,4
3	0,4	10,8	3	3,2	10,0
5	2,0	11,2	5	5,0	10,5
10	2,1	10,8	11	7,0	10,2
13	2,2	10,5	13	8,8	10,0
17	2,3	10,4	17	9,1	9,2

In order to study the effect of different dose rates on the formation of the grafted copolymer, the grafting was carried out in the presence of methyl alcohol vapors at dose rates of 11, 68, and 100 rad/sec, with irradiation doses ranging from 0.12 to 7.20 M/rad (Table 5). From the obtained data, it follows that with an increase in the irradiation duration, at all dose rates, both the grafting yield and the content of PVD<sub>2</sub> in the grafted copolymer increase. The increase in irradiation duration is due not only to the continuous progression of grafting over time but also to the radiation stability of the grafted PVD<sub>2</sub>.

As seen from Table 6, as a result of irradiation, with an increase in the integral dose, the H/C fabric significantly loses its whiteness, and the higher the absorbed irradiation dose, the greater the decrease in whiteness degree. When irradiating cotton/linen fabric in a methyl alcohol vapor environment, this effect is only slightly reduced. For example, for the initial H/C fabric, this value is 79%, while for the irradiated fabric at 69.5% Mr, this value increases to 88.9% for the grafted copolymers. For the irradiated

fabric in the presence of methyl alcohol vapors under the same conditions, the whiteness degree is 86.2%.

The results of the change in water vapor sorption at 50% relative humidity of grafted copolymers of C/F and H/C with VF<sub>2</sub> are presented in Table 7. From the data provided, it is evident that as the content of PVD<sub>2</sub> increases, the sorption values gradually decrease.

Table 7 presents the results of the study on the mechanical properties of viscose fabrics irradiated in vacuum and in the presence of methyl alcohol vapor, as well as their grafted copolymers obtained under identical conditions. As seen, the properties of the irradiated fabrics, both in the vacuum and in the methyl alcohol vapor environment, are relatively similar. At an integral irradiation dose of 1.62 Mrad, these values remain almost unchanged. As the irradiation dose increases, the tensile strength and elongation decrease slightly. The loss of fabric strength under radiation is also due to the loosening of the cellulose structure [9] and the partial destruction of intermolecular hydrogen bonds [10]. For the grafted copolymer of H/C fabric with PVDF

obtained under the same conditions, the decrease in strength is observed to a lesser extent compared to the fabric modified by the grafting of PVDF. This result is related to the nature of the grafted polymer. It is possible to assume that during the grafting of VF under the continuous action of gamma rays, a large amount of hydrogen fluoride is formed. In this case, an acceleration of the cellulose loosening process is observed, and on the other hand, the higher the content of the grafted polymer, the greater the possibility of the disorienting arrangement of chains in ordered regions, which leads to further weakening of intermolecular bonds.

To study the effect of the dose rate on the changes in the physical-mechanical properties of the fibers, we investigated the changes in the strength and elongation of H/C fibers irradiated in a vacuum and in the presence of methyl alcohol vapor at a dose rate of 90 rad/sec over a wide irradiation time range, as well as their grafted copolymers with PVDF obtained under identical conditions. As seen from the data in Table 8, the strength of the irradiated fibers significantly worsens with an increase in irradiation duration, while the reduction in breaking elongation is less pronounced than the reduction in strength. However, this effect is more noticeable in fibers irradiated in a vacuum. The grafted copolymer obtained under the same conditions loses even more strength.

Table 8: Weight loss of the original, irradiated and modified G/C with PVDF within 12 hours at 230°C, %.

Irradiation duration, hours	Irradiated Samples	Grafted Copolymers	
	Weight Loss	Content of PVF <sub>2</sub> , %	Weight loss, %
In the vacuum			
Initial	10,1		10,1
5	10,5	3,3	9,0
10	10,9	4,4	8,2
15	11,2	4,7	8,0
18	11,9	7,2	6,8
		9,0	4,3
In the air			
Initial	27,6	7,2	20,8
18	31,9	9,019,7	
In the vacuum			
Initial	25,1		
22	29,3	7,2	21,7

The obtained results are presented in Table 8. When irradiating H/C in both a vacuum and in the presence of methyl alcohol vapors, its weight loss

slightly increases. This effect is explained by destructive processes that lead to the formation of labile points in relation to the effect of elevated temperatures.

### 3 CONCLUSIONS

Radiation grafting of vinylidene fluoride was performed under various conditions on cotton cellulose, hydrated cellulose, and fabrics based on them in order to improve the most significant physical and chemical qualities and impart new ones. The effects of solvent type and radiation dose rate on the grafting procedure were investigated. The findings demonstrated that the grafting rate and yield increased while decreasing as the dose rate increased. The dosage rate and the grafting rate are proportionate. Due to the hydrophobicity of the modifying polymers, it was found that the sorption and swelling capacities of samples in water increase as the concentration of grafted fluorine-containing polymers increases. Graft copolymers of cellulose and fluorinated polymers have been demonstrated to have improved thermal stability. Additionally, the quantity of weight loss reduces and the decomposition temperature rises with increasing grafted polymer concentration.

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