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Strengthening the Clumping Paper Properties using Hydroxypropyl Cellulose Applied on a Historical manuscript 13th Century AD.

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Abstract: The main objective is to find a suitable and effective solution to strengthen agglomerated paper fibers and improve their physical, mechanical, and chemical properties. Many reasons lead to petrification and sticking papers. The alone worker can't lead to petrification and damage because all deterioration factors participate in the provisions of the damage circle on papers. The possible end is the loss of parts or parts or the annihilation of the entire manuscript or book. Given the archaeological and artistic value of the paper manuscripts, hydroxypropyl cellulose was chosen because it is a paper-friendly material. The papers are subject to artificial aging to reach an age like the age of the fossilized manuscript. Then the samples were naturally aged by infecting them with *A. niger* until they reached adhesion and agglomeration. After that, a separation process was carried out for the leaves. The leaves were consolidated with 2% hydroxypropyl cellulose. Then, an evaluation was carried out to determine the effect of hydroxypropyl cellulose on paper using digital microscopy, scanning electron microscopy, mechanical properties measurement, color change measurement, FTIR measurement, and pH measurement. The results of the examination and evaluation revealed its success in strengthening the papers and improving their properties. Therefore, it was applied to manuscript papers dating back to the thirteenth century AD.

Keywords: hydroxypropyl cellulose; leaves; paper; manuscript; FTIR.

1. Introduction

Many libraries and preservation houses around the world contain rare manuscripts and books. Many papers suffer from fossilization and deterioration resulting from poor preservation and lack of periodic conservation [1,2]. The reasons leading to this phenomenon are many and multiple, such as the difference and variation in temperature, moisture, and the effect of microorganisms [3-5]. In addition to the effect of the internal components involved in the composition of paper, such as the effect of lignin and some additives and fortifiers, such as the use of animal glue [6]; Lignin is affected by light, which leads to the yellowing of the paper and cracking of the cellulose fibers into short units, and leads to the appearance of yellow and brown spots in the areas exposed to light [1-2], it was common for some paper made by hand in Europe until the beginning of the nineteenth century to be reinforced with a layer of animal glue, and thus this paper became composed of two layers, the first layer of fibers that make up the main component of the paper, and the second layer of animal glue, which has become a

great danger as a result of being damaged by different temperatures and moisture because they act as the adhesive that leads to the cohesion and adhesion of the papers to each other [1-3]. Fungi degrade cellulose by enzymes [7-12]. Enzymatic activities are divided into three categories: There are two types of endoglucanases: endoglucanases and 1,4-D-glucan-4-glucanohydrolases (EC 3.2.1.4), exoglucanases, such as 1,4-D-glucan glucanohydrolases, are two types of exoglucanases [7], 1,4--Dglucan cellobiohydrolases (cellobiohydrolases) (EC 3.2.1.74) and cellodextrinases (cellodextrinases) (EC 3.2.1.74) (EC 3.2.1.91),-glucosidases (EC) and -glucoside glucohydrolases (EC) Endoglucanases randomly cut internal amorphous sites in the cellulose polysaccharide chain [5,12,13], resulting in oligosaccharides of varying lengths and, as a result, novel oligosaccharides the end of the chain Exoglucanases have a processive action on the exoglucanase. Cellulose polysaccharide reducing or nonreducing endings chains, with the principal products being glucose (glucanohydrolases) or cellobiose (cellobiohydrolase). Exoglucanases can operate on microcrystalline cellulose as well, probably exfoliation it. The microcrystalline structure's cellulose chains (672). Glucosidases are enzymes that break down soluble cellodextrins and cellobiose to glucose [14-17].

HPC is a non-ionic, water-soluble cellulose ether with unique characteristics. It combines the aqueous thickening and stabilizing capabilities of water-soluble cellulose polymers with organic solvent solubility, thermoplasticity, and surface activity. It's made by combining alkali cellulose and propylene oxide at high temperatures and pressures. Propylene can be replaced on the cellulose through an ether bond at the three reactive hydroxyls present on each anhydroglucose monomer unit of the cellulose chain [18].

Hydroxypropyl cellulose (Klucel G) was widely utilized as a suitable pigment material consolidation material. According to (Feller and Wilt,1993) [19], larger molecular weight Klucel grades (such as M and H) are less stable than lower molecular weight grades (G and L). Conservators have employed Klucel G for matte paint consolidation, and various grades have been used in poultices, inpainting media, and infilling media. Klucel-G can be used successfully in water/alcohol solutions to consolidate pigmented ethnographic materials with matte surface quality and in ethanol to consolidate darker colors like the blues and browns of water-based paints that are sensitive to aqueous consolidates (i.e., darken) [20].

This study aimed to see if cellulose nanocrystals might be used as a consolidation material to improve paper's mechanical and chemical qualities.

2. Materials and Methods

2.1. Paper samples.

The experimental studies were first carried out on Whatman filter paper No. 1 that had been infected with *A.niger*, resulting in the sticking and petrification of the leaves. This is the same situation as the manuscript from the thirteenth century AD that served as the basis for the empirical study, and it was then de-sticked using the cellulase enzyme [1]. For three weeks, the samples were subjected to accelerated artificial aging at a temperature of 80°C and relative humidity (RH) of 65 percent in a closed climatic chamber, equivalent to 75 years of natural age [21]. The ISO 5630-3:1996 standard was followed during the aging process.

2.2. Preparation and application of hydroxypropyl cellulose.

Hydroxypropyl cellulose was chosen as consolidation, and CTS supplied it. It was prepared in a concentration of 2%. Consolidate dissolved in ethyl alcohol (ethanol) (2%) [22]. The consolidation was applied to the paper samples and manuscript paper using a soft brush.

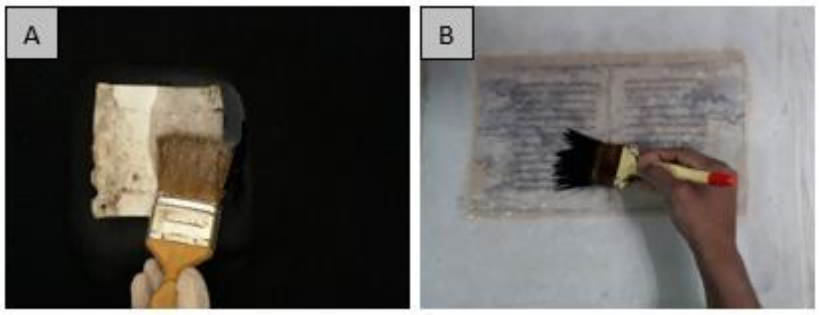

Figure 1. Application of Hydroxypropyl cellulose, (**A**) Filter paper, (**B**) A historical manuscript.

2.3. Evaluation of the strengthening treatment efficiency.

2.3.1. Mechanical behavior measurements.

Before measuring tensile strength and elongation, the samples were conditioned for 24 hours in a standard environment (23°C and 50% RH). Tensile and elongation measurements were performed on 15mm wide strips between jaws set 100mm apart [23, 24], using QMat 5.37, Tinius Olsen, according to Standard No. EN ISO 13934-1; 1999 Maximum Force & Elongation-Strip Method.

2.3.2 The color change measurement.

The color change in the treated papers has been measured in accordance with International Commission on Illumination color space (CIE l*a*b*) system using Ultra-scan PRO, Hunter lab, USA, UV spectrophotometer, which has been characterized by Rushdy *et al.* (2017) [24], Fouda *et al*. (2019) [25] and Abdel-Maksoud and Marcinkowska (2000) [26]. The L* value was calculated by comparing darkness to light, The a* value was used to compare red and green colors, and the b* value was used to compare yellow and blue colors. The overall color difference (E) was determined using the following formula:

$$\Delta \in * = \sqrt{(\Delta \boldsymbol{l}*)\mathbf{2} + (\Delta \mathbf{a}^*)\mathbf{2} + (\Delta \mathbf{b}^*)\mathbf{2}}$$

The difference between the values of l*, a*, and b* for the reference and treated samples were used to derive the results of L, a, and b. [27].

2.3.3. Digital microscopy.

For the surface morphology of the paper, writing inks, and color paints, as well as assessing the paper-making techniques employed to create the illuminations, a handheld digital microscope (ASIN: HJH001 B083TGGVPB) at 0x-1600x magnification was used [28]. The lens was a 0.3m CMOS Sensor with an aperture of 2.0 MPIX.

2.3.4. Scanning electron microscopy.

The samples were examined under a scanning electron microscope at the Agriculture Faculty, Cairo University, Cairo, Egypt.

2.3.5. Fourier-transform infrared spectroscopy.

The analysis of Fourier transform infrared (FTIR) for the untreated and treated samples have been examined using a spectral resolution of 4 cm-1 and high-resolution attenuated total reflection - Fourier transformation infrared spectroscopy (ATR-FTIR) on a JASCO FT/IR-4700 Spectrophotometer from Japan.

2.3.6. pH measurement.

The pH was considered the most important factor; the stability of papers toward natural and accelerated aging was determined by using the pH measurement. Cold extraction measurements were carried out according to the Tappi method [29] using Thermo Scientific Orion Star A111pH Benchtop Meter.

3. Results and Discussion

3.1. Assessment of the historical manuscript.

This manuscript dates to the 13 century AD and is in a poor state of preservation kept in Al-Azhar Library in Cairo. It has reached severe damage, leading to its leaf agglomeration. The reason for this is due to many factors, including the constant difference in temperature and humidity, in addition to the influence of fungi and the materials included in its composition. It consists of a multilayer. It was made up of mechanical support (paper), writing (painting) layers (black ink, red ink, Arabic gum), an Arabic gum layer to connect the ink to the support, and a starch sizing layer to preserve the ink. Each writing or painting is distinct, and identifying and describing its materials can expose and validate its history, including the creative artistic process and/or the time period in which it was created (Figures 2 a and b).

Figure 2. The clumping paper of historical manuscripts under investigation.

3.2. Digital microscopy.

Before treatment, the results of positive control and manuscript samples (Figures 3 c and e) showed leaves color change, fiber weakness, and dry leaves. This damage led to the loss of paper's mechanical, physical, and chemical properties.

After treatment with Klucel G (Hydroxyl Propyl Cellulose 2%), the examination results illustrated that the fiber became very strong and smooth, an improvement in the properties of

the paper, especially the natural properties, compared to the positive control (Figures 3d and f).

3.3. Scanning electron microscopy.

The filter paper and manuscript fibers were very clear, smooth, and strong, and the distances between fiber structures were close [24]. The samples treated with hydroxyl propyl cellulose2% showed individual crosslinking that resulted in being covered with the polymer used. The penetration of hydroxyl propyl cellulose 2% between the fiber structures of book paper was very good (Figures 4 a, b, c, d, e, and f).

3.4. Mechanical behavior measurements.

Hydrogen bonds hold old paper fibers together, influencing the distance between crosslink fibers. The interfiber connection relies heavily on water molecules. The free water produces the paper to weaken, manifested by the wet strength of the paper. Table 1 shows that the mechanical strength of the filter paper consolidated by hydroxyl propyl cellulose2% improved the strength of the clumping paper. This is attributed to the hydroxyl propyl cellulose 2% not only increases the fiber bond and consequently increases the hydrogen bond between fiber but also is less water absorbent.

Table 1. Shows the effect of hydroxyl propyl cellulose 2% on the mechanical properties of clumping papers.

Time	Reference Maxim-um Force N	Negative Maximum Force N	Positive Maximum Force N	Treatment Sample Maximum Force N	Reference Elongation %	Negative Elongation %	Positive Elongation %	Treatment Sample Elongation %
1 week	34.49	3.708	4.987	13.30	1.524	1.711	2.312	1.286
2 weeks	34.49	9.64	10.74	11.46	1.524	0.775	2.241	1.193
3 weeks	34.49	7.22	9.149	31.28	1.524	1.004	1.3275	0.889

3.5. Measurement of color change.

The effect of hydroxyl propyl cellulose 2% treatment on fossilized paper color change was investigated, and the results were shown in a Table. 2. The l*-value results showed that the treated samples were nearly white for all weeks. These results are the same reference and negative control.

Table 2. Measurement of color change for the hydroxyl propyl cellulose2% treated samples for different treatment periods.

Treatment	The samples after seven days				The samples after fourteen days				The samples after twenty-one days			
	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
Standard	90.42	-0.20	0.70	0.00	90.42	-0.20	0.70	0.00	90.42	-0.20	0.70	0.00
Negative Control	80.07	0.22	7.96	12.65	77.94	0.25	10.69	16.00	76.36	0.90	5.72	14.97
Positive Control	80.44	0.81	6.17	11.42	76.19	1.03	6.07	15.26	79.80	0.65	6.34	12.06
Sample treated with HPC.	85.37	-0.43	7.02	8.09	77.05	0.99	4.58	13.97	79.63	0.67	4.81	11.58

The results of the a*-value indicated that the color of the samples of the first and the third week, which were treated with hydroxyl propyl cellulose 2% tended to the green color for all weeks and compared with positive control [30]. On the other hand, the results of the b*-value of the samples before treatment by hydroxyl propyl cellulose2% was near dark yellow, but after treatment for three weeks. The reference standard sample's and the negative control

sample's color tended to be their natural hues (yellow color). This result agreed with those presented by Atodiresei *et al.* (2013) [31].

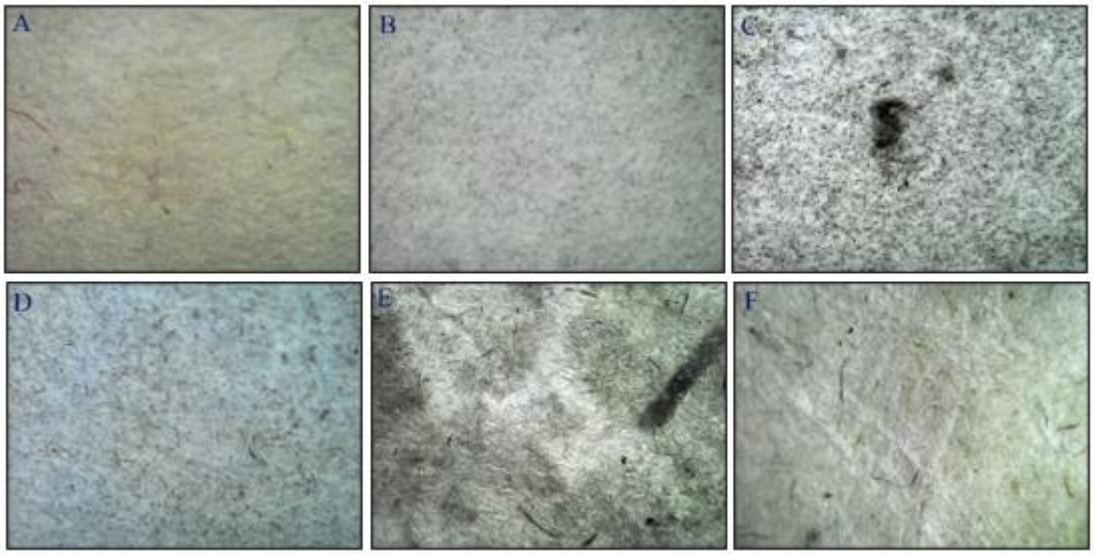

Figure 3. A digital microscope image (magnification of 1600x) of various Whatman paper samples (**A**) Standard Whatman paper, (**B**) Whatman filter paper negative control, (**C**) filter paper positive control before hydroxyl propyl cellulose 2% treatment, and (**D**) after hydroxyl propyl cellulose 2% treatment in addition to the clumping paper manuscript (**E**) before and (**F**) after hydroxyl propyl cellulose 2% treatment.

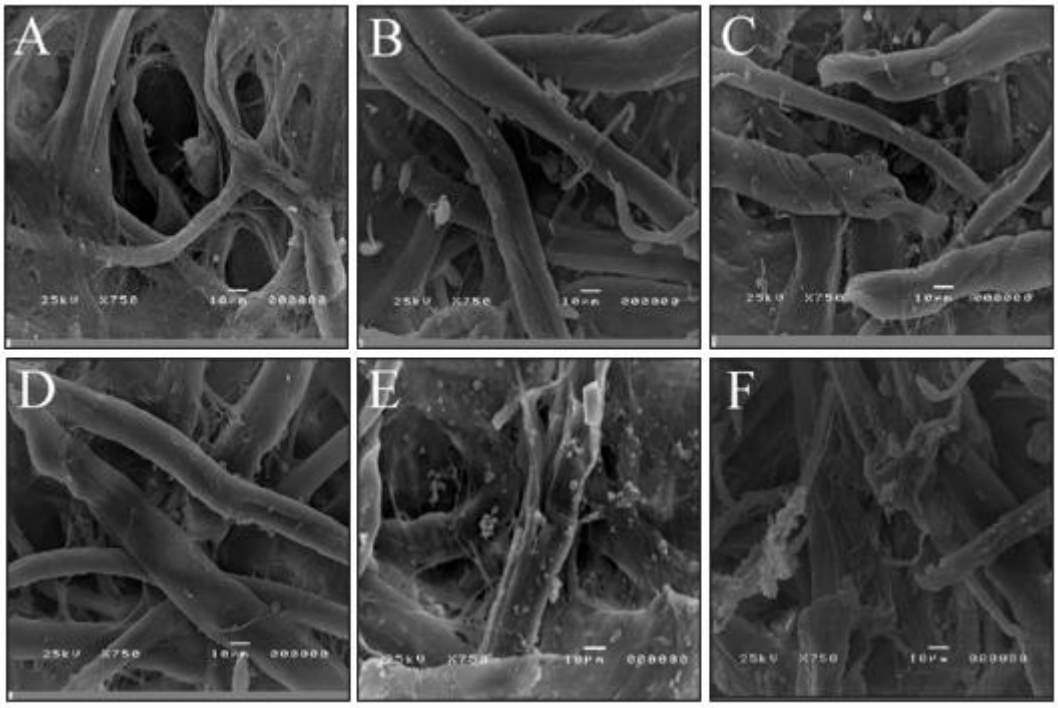

Figure 4. Scanning electron micrographs of various Whatman paper samples (**A**) Standard Whatman paper, (**B**) Whatman paper negative control, (**C**) Positive control of filter paper before hydroxyl propyl cellulose 2% treatment and (**D**) after hydroxyl propyl cellulose 2% treatment in addition to the clumping paper manuscript (**E**) before and (**F**) after hydroxyl propyl cellulose 2% treatment.

The findings indicate that the second-week samples treated with hydroxyl propyl cellulose 2 percent showed a minor color change (E), although the first and third weeks showed good outcomes.

3.6. Fourier transform infrared spectroscopy.

The discrepancy in intensity and absorption levels was observed during the examination process. For the first, second, and third weeks, comparisons of the treated sample with reference, negative, and positive control samples were shown in (Table.3; Figures. 5a, b, and c). The results showed O-H stretching decreased after 7 and 21days at 3331.43cm−1, 3328.53 cm−1,3289.96 cm−1,3282.25 cm−1 [32], but the second week increased at 3331.43 cm^{-1} and 3285.14 cm^{-1} [33]. the decreasing or the increasing intensity for all weeks was beside the reference and negative control.

The stretching bands (CH_2) and (CH) located at 2897.52cm^{-1}, 2898.49cm^{-1}, and 2887.87cm^{-1} were slightly modified. They become intensely decreasing after 7 and 21 days. The decrease in the intensity was slighter than the reference and negative control samples, leading to an increase in the amorphous regions [34].

Table 3. Result of the FTIR analysis.

Function Groups	Reference		Negative Control		Positive Control		The sample treated by hydroxyl propyl cellulose2%	
	Absorbance Region	Intensity	Absorbance Region	Intensity	Absorbance Region	Intensity	Absorbance Region	Intensity
The samples after seven days								
O-H Stretching	3330.46	36.18	3330.46	52.44	3330.46	29.49	3331.43	23.87
	3290.93	36.69	3274.54	53.34	3287.07	30.21	3289.96	25.01
C-H Stretching	2887.88	64.60	2895.59	74.97	2898.49	56.41	2897.52	48.78
O-H bending of adsorbed water	1644.02	78.23	1643.05	98.21	1643.05	89.34	1644.98	90.17
CH_2 bending	1426.1	81.25	1427.07	96.18	1427.07	86.12	1427.07	83.79
O-H in-plane bending of amorphous cellulose	-	-	1333.53	93.91	1333.53	82.34	1333.53	79.06
CH_2 bending	1314.25	78.96	92.24	92.24	1315.21	79.90	1315.21	76.89
C-O-C	-	-	900.59	96.02	-	-	-	-
The samples after fourteen days								
O-H Stretching	3330.46	36.18	3330.46	41.81	3330.46	32.08	3331.43	36.13
	3290.93	36.69	3274.54	42.65	3289.96	32.81	3285.14	36.88
C-H Stretching	2887.88	64.60	2889.81	69.18	2887.87	59.86	2898.49	60.92
O-H bending of adsorbed water	1644.02	78.23	1643.05	86.03	1642.08	90.51	1644.02	89.66
CH_2 bending	1426.10	81.25	1426.1	86.85	1426.10	86.73	1427.07	87.06
O-H in-plane bending of amorphous cellulose	-	-	1332.57	85.15	1332.57	83.58	1334.5	85.02
CH_2 bending	1314.25	78.96	1314.25	83.21	1314.25	81.34	1315.21	83.03
C-O-C	-	-	-	-	899.62	86.05	-	-
The samples after twenty-one days								
O-H Stretching	3330.46	36.18	3331.43	42.10	3329.50	38.41	3328.53	32.79
	3290.93	36.69	3279.36	43.01	3274.54	38.32	3282.25	33.57
C-H Stretching	2887.88	64.60	2889.81	74.20	2899.45	60.67	2887.87	54.92
O-H bending of adsorbed water	1644.02	78.23	1643.05	86.22	1643.05	85.01	1644.01	88.61
CH_2 bending	1426.1	81.252	1427.07	85.84	1427.07	86.54	1426.10	85.13
O-H in-plane bending of amorphous cellulose	-	-	1332.57	83.32	1334.50	85.45	1333.53	82.34
CH_2 bending	1314.25	78.96	1314.25	80.87	1314.25	83.61	1314.25	80.62
C-O-C	-	-	-	-	-	-	-	-

There were also some changes at 1644.98cm^{-1}, 1644.02 cm^{-1}, and 1644.01 cm^{-1} regions for the first, the second, and the third week respectively. These regions express about δ (OH). The first and second weeks witnessed a decrease in intensity, but the increase in intensity was in the third week. In any case, whether the increase or decrease in intensity is close to the same reference or negative control [35, 36]. We can make a remark about increasing in the stretching band CH_2, which has been located at 1426-1427 cm ^{1}. They become increasing regions according to these regions express the cellulose crystallization, especially whenever the value approaches 1430 cm^{-1} [37].

We can distinguish the cellulose crystalline and amorphous by comparing the O-H stretching represented by the amorphous located at 1333.53 cm^{-1}and the stretching band of CH_2 expressing the cellulose crystalline located at 1314.25 cm^{-1}. All samples marked by intensity increasing for 1315.21 cm^{-1} region) [38].

About the 900–1200 cm^{-1} region related to the fingerprint of cellulose, it should be noted that no significant changes were detected in all weeks of aging [39-41].

The previous FTIR results confirmed that hydroxyl propyl cellulose 2 % made the fibers more strong and durable and did not affect their physical and mechanical properties, as evidenced by the intensity values of the treated sample, which approached the same intensity values of the standard sample, while the positive sample suffered from a loss of its physical and mechanical properties.

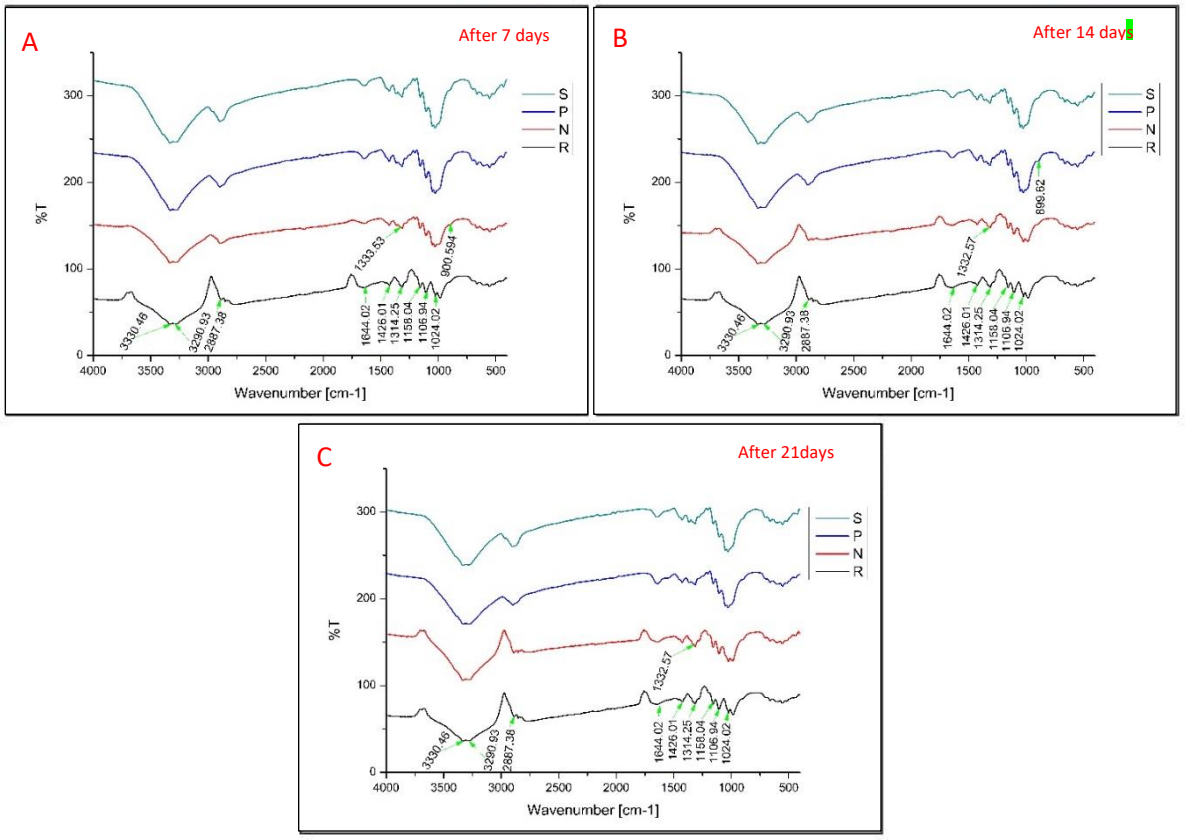

Figure 5. The FTIR spectra of filter paper samples in which R is the reference, N - the negative control, P - the positive control, and S - a hydroxyl propyl cellulose 2% treated.

3.7. pH measurement.

After hydroxyl propyl cellulose 2% treatment, pH tests of the filter paper revealed that the treated paper tended to neutralize to the same degree as the reference and negative control samples after 7 and 21 days, but the second week tended to decrease (Table 4).

Table 4. pH measurement results.

Treatment	After 7 days	After 14 days	After 21 days
Reference	6.80	6.80	6.80
Negative Control	6.51	6.54	6.76
Positive Control	6.87	6.67	6.52
The sample treated by hydroxyl propyl cellulose 2%	6.80	6.76	6.80

4. Conclusions

Despite the weakness of the lumpy leaves after separating them, which makes it difficult to complete the rest of the treatment stages, strengthening them with hydroxypropyl cellulose2% (Klucel G) has improved their natural, mechanical, and chemical properties, which was confirmed by the results of the examination and analysis.

The results of the optical examination, digital microscope, and scanning electron microscope, in addition to the results of measuring the color change, proved that there was no color change, sedimentation, or dimension change in the leaves because of the hydroxypropyl cellulose2% (Klucel G) strengthening it. The results of measuring the tensile and elongation forces revealed an improvement in the natural properties of the paper at different times. The results of FTIR analysis revealed that the lost water content was returned to the leaves.

In the end, hydroxypropyl cellulose2% (Klucel G) is considered a good material for strengthening agglomerated papers because it is made of the same basic component that is included in the composition of paper, which is cellulose.

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Conflicts of Interest

The authors declare no conflict of interest.

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