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Consolidation of the Paper Works with Cellulose Nanofibers

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Abstract: Consolidation is considered as an important step in the conservation of cultural and historical documents and books and the main purpose is to emphasize the strength of the paper support. Consolidant materials are used in the restoration of paper cultural heritage in order to improve the strength of the paper structure, which has decreased due to the passage of time and also the impact of environmental factors. Paper works are gradually degraded by various destructive factors due to their structural properties. For this reason, it is necessary to applying consolidation treatments for strengthening of degraded paper. The purpose of this research is to evaluate the effect of cellulose nanofibers and its use as a consolidant agent to restore durability to paper works. In this study, to consolidation of the paper, cellulose nanofibers with a concentration of 1% by weight were prepared as a suspension with water and used to treat the samples. In order to evaluate the effect of treatment, the samples were exposed to dry-heat and moist-heat aging and pH, colorimetric, and tensile strength tests were performed before and after aging. The results showed that the pH of the samples increased after treatment with cellulose nanofibers. After dry- heat and moist-heat aging, the pH of the samples decreased slightly. Cellulose nanofiber treatment increased the tensile strength of the samples. However, after two stages of aging, the tensile strength of the samples has decreased compared to the previous stage. The use of cellulose nanofiber treatment made the color of the samples brighter but after aging, the brightness of the samples decreased.

Keywords: Cellulose Nanofibers, Paper Restoration, Consolidation, Moist-Heat Aging, Dry-Heat Aging, Nanotechnology

1. Introduction

Paper plays an essential role in the cultural and economic development of humanity. Books, manuscripts, printed copies, archival documents are precious treasures that must be preserved and passed on to the next generation. Due to their organic structure, paper relics have high sensitivity and susceptibility to harmful factors and are always exposed to damage. These effects are stained discolored, discolored and torn, or attacked by insects due to physical, chemical and biological destructive factors, while, the materials used to treat them can be very effective as a secondary injury in increasing the rate of these complications [1].

From the point of view of theoretical foundations of restoration, the materials used to treat paper relics should have desirable physical properties and over time, these properties should have maximum durability and stability. Also, from the point of view of physical properties, the most suitable materials for the treatment of paper relics should always have two important criteria, namely transparency and durability against aging [2]; In addition, the materials used to treat paper works must be compatible with their original structure. [3]. Consolidation treatments are usually used to prevent paper degradation. Consolidant materials are usually organic or mineral materials that are used to increase the strength of other materials [4].

In fact, consolidant refers to materials that have the ability to penetrate the structure of an effect and bind damaged particles together and also increase resistance to external attacks [5]. Consolidation treatments with the aim of replacing the lost lining agent, improving the mechanical properties and strength of the sheets of paper, preventing the compound from spreading on the surface of the paper, increasing paper resistance against acids and oil penetration, improving paper flexibility, reducing sticky dust on the surface of the effect. In order to consolidation paper works, different materials or films are used to improve their mechanical properties. This process can be done in a total or partial way [6].

Consolidant materials must have common characteristics such as sufficient bond strength, inertness and chemical activity with the substrate, aging resistance, color fastness and reversibility. While polymer adhesives, which are used as consolidant materials, have various disadvantages; among other things, they cause yellowing and discoloration of paper after aging, they have little resistance to biological agents, as a result of using water as a solvent for them, they cause the surface of paper works to wrinkle, increase the water absorption of the paper surface, they reduce the flexibility of the paper, their strengthening effect decreases with time. In general, these materials cannot protect the paper structure in the long term [2].

Therefore, due to the importance of these materials and their application in the protection of paper relics, various materials have been suggested by researchers to treat paper works that have little or no strength. Also, many studies have been done to identify the characteristics of these materials and their effect on paper. Each of the consolidant materials used for paper works, along with their advantages, also have disadvantages that can limit their use [7, 8]. Restrictions on the use of previous materials have led researchers to study new materials and methods to achieve optimal protection [9].

On the other hand, from recent decades to date, the use of nanomaterials technology has attracted a lot of attention among researchers in the field of restoration and conservationists in the field of prevention of erosion and treatment of paper relics [10]. The idea of using nanomaterials to increase the performance of paper and cardboard includes all the properties and functional properties of paper, from improving optical properties to enhancing weathering properties and enhancing mechanical and strength properties [11].

The properties of paper can be improved in different ways, such as adding nanomaterials to pulp suspension or coating paper with nanomaterials. Cellulose-based nanomaterials are more useful due to their special characteristics of resistance and safety in use due to their biodegradability [12]. Cellulose nanofibers have a variety of properties due to their high diversity [13]. The physical and mechanical properties of cellulose nanofibers are almost certain. These characteristics of cellulose nanofibers have been investigated in the research of paper and polymer industries [8, 14, 15]. These properties have been evaluated in studies of other sciences including paper and polymer industries [3, 16, 17].

The use of cellulose nanofibers along with environmental concerns as a reinforcement in resins have significant advantages over other materials, such as biodegradability, availability, low cost, high flexibility and spatial properties, physical properties. Notable, high transparency, chemical purity and biocompatibility, chemical stability and durability of properties, low energy consumption and relatively active surface for bonding special groups [18-21].

Few researches have been done in the field of using cellulose nanofibers to restoration historical paper works. A film has been made using cellulose nanofibers and 5% hydroxypropyl cellulose in ethanol, which can be a suitable solution for restoration torn photographic films and slide shows. [22]. The film made with cellulose nanofibers and 5% hydroxypropyl cellulose in ethanol has good stability against light aging and moist-heat aging. The transparency of the film has not changed since the filming. These films shrink due to direct contact with water, but do not change at high temperature and fluctuations in relative humidity. Also, after use, they are easily removed from the paper and do not leave any residue. This film has shown the best features for repairing tears in slide shows [23].

The use of bacterial nanocellulose and cellulose nanofiber suspension has led to the restoration of mechanical damage such as tears and missing parts, as well as strengthening the weakened parts of historical papers [24].

This research was conducted with the aim of evaluating the material of cellulose nanofibers and its use as consolidant to strengthen and also to reduce physical changes in paper effects. Paper is highly vulnerable due to its organic structure, and if the strength and durability of the paper is reduced and not confronted, irreparable damage will be done to the structure of the paper, which will cause the loss of the properties of this material and in it will eventually disappear completely.

Hence, the necessity and necessity to deal with it is obvious. For this purpose, this research seeks a treatment to strengthen the mechanical and appearance characteristics, reaction in the environment of degradation and during accelerated aging treatment, on historical paper relics. Due to the properties of cellulose nanofibers and since the effect of this material in the field of protection and restoration of historical paper relics has not been studied in detail and specifically, in the present study, the use of this material as a consolidant in the field of protection and restoration of historical paper relics has been investigated.

2. Materials and Methods

2.1. Materials

In this study, in order to treat paper samples from cellulose nanofibers produced mechanically by Nano Novin Polymer Company of Iran with an average diameter of 35 nm, bagasse fibers were used. Given the possibility that direct testing of treatments on historical papers may harm them, tests are usually performed first on special cellulose papers (filter paper) and after the results are obtained, they are used for old papers.

Therefore, in this study, a standard quality paper (Monctel 393 filter paper equivalent to Watman 42 paper) was used to perform the tests due to its neutral pH and high cellulose content. In addition, the physical and chemical properties of this paper are known and its use in similar studies is common [25, 26].

In the next step, a suspension of cellulose nanofibers with a concentration of 1% by weight in water was prepared and used to treat the samples. Samples were immersed in the prepared treatment for 2 minutes. After treatment, the samples were subjected to aging and the results of the tests before aging were compared with the results after aging. Table 1 shows the code of the tested samples.

Table 1. *Abbreviation code of prepared samples.*

Sample code	Description of treatment
P	Untreated paper
PTN	Paper treated with cellulose nanofiber suspension

2.2. Methods

2.2.1. Accelerated Aging

Artificial accelerated aging was used to investigate the changes made in the samples during the aging process. The studied changes included pH changes, color changes and tensile strength of the samples. In this test, the treated samples and the control samples were aged in two ways. Moist-heat aging was performed according to TAPPI T 544 sp-03 standard at 90°C and 50% relative humidity for 384 hours [27[.

Dry-heat aging was performed according to ASTM-D776-92 standard, with a temperature of 105°C for 288 hours to compare the changes in the samples after these tests with the results before aging [28]. This test was performed using a Memmert oven with a maximum temperature of 120°C and 600 watts and 220 volts. Due to the possibility that direct testing of consolidation treatments on historical papers may damage them, the tests are performed first on aged papers and after obtaining the results, are used for historical papers.

Therefore, in this study, in order to approximate the conditions of the used paper samples to historical papers, first the paper samples were subjected to dry- heat aging and moist-heat aging according to the mentioned standards, and then to perform the desired tests, were used.

2.2.2. pH Measurements

ISO 6588-1 (cold extraction method) was used to check the changes in the pH of the samples before and after aging. This test was performed using Metrohm 744 digital pH meter [29].

2.2.3. Colorimetric Analysis

In this test, color changes in the samples were measured in the stages before and after aging by means of color tecto alpha handheld colorimeter, a product of Salutron messtechnik company. This test was performed based on the CIE system and according to the ISO 11644-4 standard. In CIELAB colorimetry method, the values of L (light-dark), a (red-green) and b (yellow-blue) are shown [30]. The changes of these factors in the samples were done according to the following equation (Eq. 1).

$$\Delta E_{\text{Lab}} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \quad (1)$$

In this equation, L^*_1, a^*_1 and b^*_1 demonstrate samples without agingand L^*_2, a^*_2 and b^*_2 demonstrate those after the aging process, also ΔL^*, Δa^*, Δb^* and ΔE^* shows the total changes of colors in the CIElab.

2.2.4. Tensile Strength Measurement

In this test, the ISO 1924-3 standard was used to measure the changes in the tensile strength of the samples in the stages before and after aging. To perform this test, paper samples with dimensions of 150 x 15 mm were prepared and 100 mm of the length of the samples were placed between the two jaws of the machine and tensile force was applied to them [31]. The tensile strength of the samples was calculated according to formula number 2 mentioned in the standard (Eq. 2).

$$\sigma_T^b = \frac{\bar{F}_T}{b} \quad (2)$$

In this equation, σ_T^b is tensile strength in (kN/m) unit, $\bar{F}_T$ is the average of maximum tensile force in N unit, and b is the width of sample in mm unit.

3. Results and Discussion

3.1. Results of Colorimetric Study

Figure 1 shows the changes in factor L (light-dark) of the samples before and after dry- heat aging and moist-heat aging. As can be seen in the diagram, the treated samples did not show any change compared to the untreated samples before aging, and after the samples were treated with cellulose nanofibers, the brightness of the paper remained almost constant. Aging of the samples caused a slight decrease in the brightness of the paper. Samples treated after dry- heat aging have similar results compared to samples treated after moist-heat aging (Table 2).

Many products of the paper aging process, such as oxidation products, cause the paper to become cloudy. As paper ages, its color changes and opacity increase [32]. Yellowing of paper materials as well as a decrease in its brightness in aging, as a result of paper decomposition due to accelerated aging. Aging causes the oxidation of cellulose and the formation of carbonyl chromophores [33].

The results show that the treatment of the samples with cellulose nanofibers before and after dry- heat aging and moist-heat did not cause a significant change in the brightness of the samples.

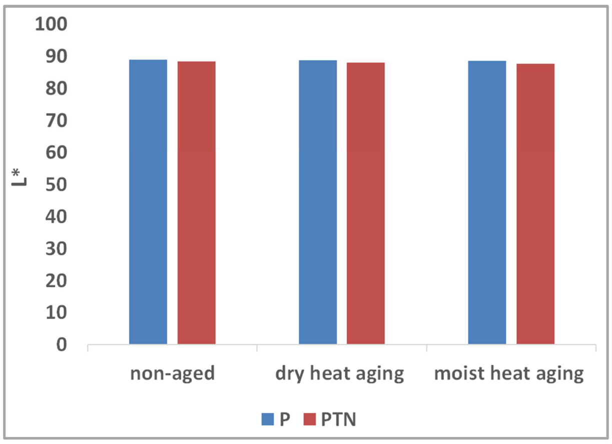

Figure 1. *The effect of using cellulose nanofiber treatment on L factor changes (light-dark) of samples.*

In colorimetry, the more positive the factor a^* (green-red) changes of the samples, the redder the sample becomes, and if it becomes more negative, it means that the color of the sample tends to be green. The results showed that the treatment of paper with cellulose nanofibers increased the factor a^* and the tendency of the samples to be red. As a result, the color of the samples has darkened (Figure 2).

The results indicate that with dry- heat aging and moist-heat factor a^* increased in untreated control samples and treated samples and some redness was added. The highest amount of factor a^* belongs to the samples treated with cellulose nanofibers after moist-heat aging. The lowest value of factor a^* is related to the control samples without pre-aging treatment.

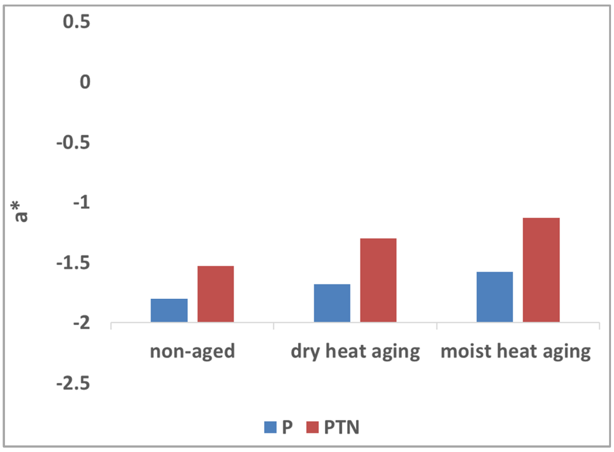

Figure 2. *The effect of cellulose nanofiber treatment on factor a (green-red) changes in samples.*

What is very important in examining the color changes in the samples is the changes in factor b (yellow-blue). In the study of this factor of color changes as shown in Figure 3, the results indicate that factor b decreased after the samples were treated with cellulose nanofibers, which indicates that the color of the samples became brighter. After dry- heat aging and moist-heat, factor b decreased compared to the previous step and the color of the samples became lighter. In untreated control samples, factor b increased after dry- heat aging and moist-heat and the color of the samples tended to yellow and became darker.

However, the amount of yellowing after aging can be due to chemical changes in the paper during the aging process, which is the same as oxidation of cellulose. The oxidized groups of cellulose are yellow chromophores and increase in yellow with increasing oxidation and the carbonyl group [34]. In general, changes in factor b indicate that the treatment of cellulose nanofibers has brightened the color of the samples.

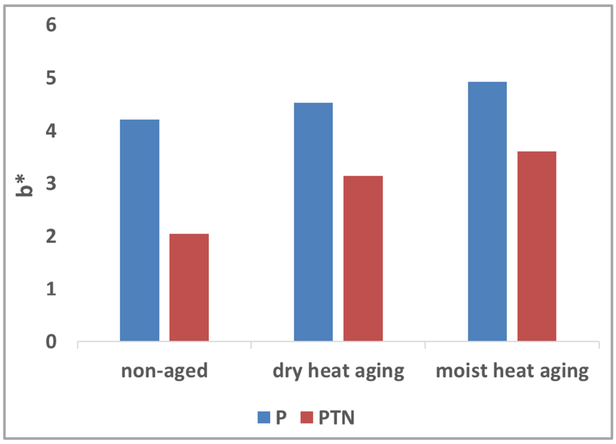

Figure 3. *Effect of cellulose nanofiber treatment on factor b (yellow-blue) changes in samples.*

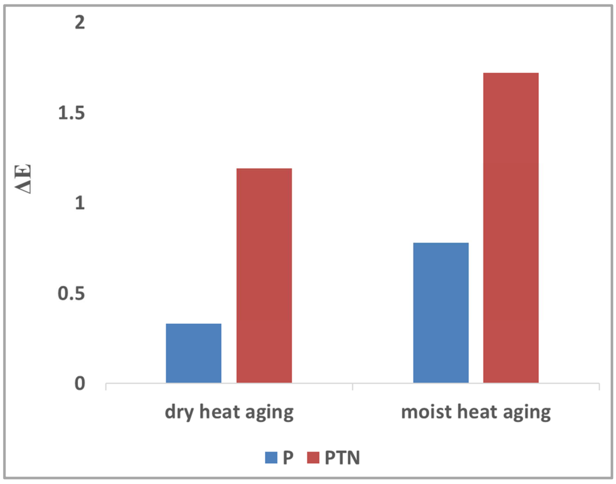

Figure 4. *Total color changes (ΔE) in the samples.*

Table 2. *Mean colorimetric factors of treated and control samples without treatment, before and after aging.*

Sample code	L^*_1	L^*_2 dry heat aging	L^*_2 moist heat aging	a^*_1	a^*_2 dry heat aging	a^*_2 moist heat aging	b^*_1	b^*_2 dry heat aging	b^*_2 moist heat aging	ΔE dry heat aging	ΔE moist heat aging
P	88.92	88.74	88.51	-1.8	-1.68	-1.58	4.21	4.52	4.92	0.33	0.78
PTN	88.38	87.86	87.54	-1.53	-1.3	-1.13	2.04	3.14	3.6	1.19	1.72

Figure 4 shows the total color change (ΔE) of the samples. The highest value of ΔE belongs to the samples treated with cellulose nanofibers after moist-heat aging. Untreated control samples showed the lowest ΔE after dry- heat aging. In general, colorimetric values (L *, a *, b *) for samples treated with cellulose nanofibers after dry- heat aging were more appropriate than the results obtained from samples after moist-heat aging. As a result, the samples treated with cellulose nanofibers showed the best colorimetric results after dry- heat aging.

3.2. Results of Tensile Strength Study

Based on the results obtained from the tensile strength test of the samples presented in Figure 5, the treatment of cellulose nanofibers has increased the tensile strength of the samples and the treated samples have higher tensile strength than the control samples without treatment. Due to the placement of the treatment material as a layer on the paper, which increases the strength.

Due to the use of cellulose nanofiber treatment, the surface area of contact between the fibers and the material has been developed, which has improved the fiber-polymer adhesion, better stress transfer to the treatment and improved tensile mechanical properties. In general, the treatment caused better interaction and mixing of the treatment material and paper fibers and this increased the strength of the samples [35].

In addition, Figure 5 shows that the tensile strength of the specimens is reduced by accelerating aging. The reduction in tensile strength of aged samples, in fact, indicates the destruction of the paper after exposure to accelerated aging, which ultimately leads to a decrease in paper strength. The highest tensile strength was related to the sample treated with cellulose nanofibers before aging and the lowest was related to the sample treated after moist-heat aging (Table 3).

Table 3. *Tensile strength of treated and control samples without treatment.*

Sample code	non-aged	TS (kN/m) dry heat aging	TS (kN/m) moist heat aging
P	1.58	1.49	1.52
PTN	1.96	1.4	1.29

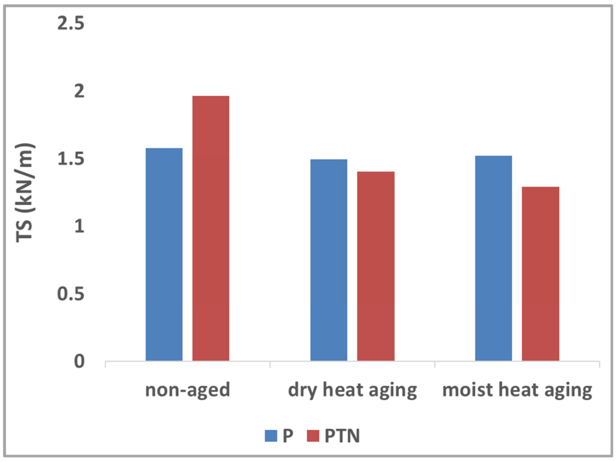

Figure 5. *Changes in the tensile strength of the samples.*

3.3. Results of pH Study

The pH changes of the studied samples are shown in Figure 6. After treatment of paper samples with cellulose nanofibers, the pH increased compared to control samples without treatment. After dry- heat and moist-heat aging, the pH of the treated samples decreased slightly compared to the previous stage, but increased compared to the untreated control samples. So that the average pH of the samples containing cellulose nanofiber treatment is 7.3 after dry- heat aging and 7.2 after moist-heat aging, respectively.

The pH of untreated control samples also decreased after dry- heat aging and moist-heat (Table 4). In general, the treatment of cellulose nanofibers increased the pH of the samples, but after aging, the pH of the samples decreased slightly. However, the samples still have a neutral pH. Of course, the decrease in pH is also caused by the accelerated aging process of paper. The decrease in pH due to aging is due to the release of H^+ ions during cellulose hydrolysis [36].

According to the results, treatment of cellulose nanofibers does not change the acidity of the paper. Accelerated aging has led to a decrease in the acidity of the samples. Exposure of paper samples to accelerated aging conditions leads to paper degradation and changes in its properties. Therefore, the reduction of acidity of aged samples is related to the degradation process. According to the pH results of the aged samples, this amount of reduction is related to the aging process and the comparison of the results indicates no destructive role and no decrease in pH after paper treatment with cellulose nanofibers on paper.

Table 4. *pH of treated samples and untreated control samples.*

Sample code	non-aged	pH dry heat aging	pH moist heat aging
P	7.27	7.15	7.03
PTN	7.48	7.3	7.2

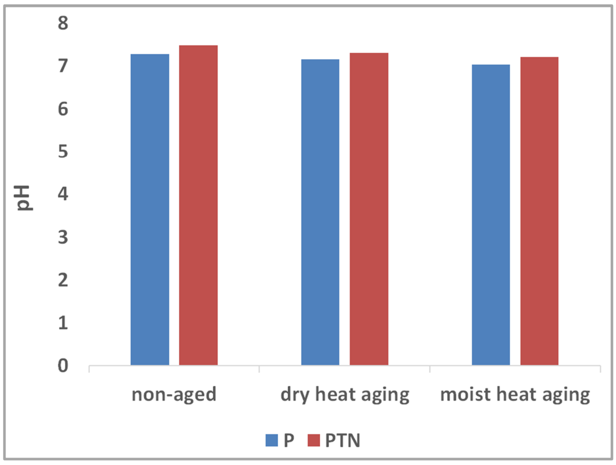

Figure 6. *pH changes of the samples.*

4. Conclusion

In this study, the effect of using cellulose nanofiber treatment on the pH, color and tensile strength characteristics of aged paper samples before and after exposure to dry- heat aging and moist-heat aging was investigated. The results showed that after treating the samples with cellulose nanofibers, the pH of the samples increased.

After dry- heat aging and moist-heat aging, the pH of the samples decreased slightly compared to the previous stage. Application of cellulose nanofiber treatment has increased the tensile strength of the samples, however, after dry- heat aging and moist-heat aging, the tensile strength of the treated samples and the untreated control samples decreased compared to the previous stage.

Cellulose nanofiber treatment made the color of the samples brighter. Aging of the samples caused a slight decrease in the brightness of the paper. This indicates that the treatment has maintained its stability. According to the results obtained from the effect of cellulose nanofiber treatment on the characteristics of pH, color and tensile strength of aged paper samples, this treatment can also be used for historical papers. Also, in addition to this treatment, alcohol treatments such as cellulose nanofiber suspension and ethanol and cellulose nanofiber suspension and isopropanol can be used to strengthen historical papers; Especially papers that contain ink and water-sensitive colors and are displaced by contact with water. In addition, the effect of these treatments on other components used in historical papers such as ink, sizing and different colors can be investigated.

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