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EFFECT OF PHYSICAL PROPERTIES OF BACTERIAL CELLULOSE NANOFIBERS BIO-COMPOSITE AS A COATING ON THE PAPER WORKS

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Abstract

The use of material with proper physical characteristics is considered a main criterion for treatment of paper works. In this study, Bacterial Cellulose Nanofiber (BCN) has been used in the form of nanocomposite into Hydroxypropyl Cellulose (Klucel-G), in order to evaluation of its physical characteristics. Klucel-G polymer is often used a common material for treatment of paper works. After preparing this Bio-Nanocomposite by using hydrosoluble casting method, were coated on paper samples by coater machine and film samples were also prepared. Paper samples color change behavior was evaluated by Reflective Spectrophotometry test (UV-Vis) and also Thermal behavior (Tg temperature) from nanocomposite dried films was studied by Differential Scanning Calorimetry technique (DSC). The results of this study showed that by adding this Nano-fiber improved Tg thermal behavior in aging conditions. As a result, the existence of this Nano-additive, as compared with pure Klucel-G, resulted in resistance against decrease of glass temperature of Klucel-G, and hence its permanence and durability. The results of Calorimetry also showed that color change behavior of paper samples was improved, because of the presence of this Nanofiber.

Keywords*: Paper work; Protection; Cellulose nanofiber; Klucel; Coating; Physical characteristic*

Introduction

The used material for treatment of paper works must necessarily have proper physical characteristics and be able to maintain these characteristics over the time, for example they must have the utmost durability. This research aims to evaluate the specific physical characteristics BCN cellulose Nanofiber as nano-additive in Klucel-G polymeric matrix (a common material for treatment of the paper works) in order to reduced physical changes of paper works as a protective coating.

Paper works are always faced to physical damages such as Yellowing and Pollution problems because of the low T_g temperature. On the other hand, may also the materials used for treatment of them, lead to the increase of these damages. Thus, one of the main problems regarding paper works is related to their physical conditions. The use of proper material for treatment of these works is of a great importance. Regarding the physical characteristics, the most proper material for restoration of paper works should always necessarily meet two demands, including legibility (transparence) and durability against aging [1], and the material used for treatment must be compatible with the main structure of paper [2]. Some studies have

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been done on the use of Nano-materials and evaluating them for treatment of paper works [3], including the use of $Ca(OH)_2$ [4-5], and $Mg(OH)_2$ nanomaterial [6], the use of polymeric nanocomposite of TiO_2-Klucel [7] and also $Mg(OH)_2$-TiO_2 nanoparticles with HEC (hydroxy-ethyl cellulose) in the form of nano multi-structure [8, 9].

Specific physical and mechanical characteristics of cellulose Nanofibers are approximately determined [10-12], and besides they have studied the physical characteristics in the form of polymeric nanocomposite including the thermal behavior [13] and high transparency [14]. The effective use of cellulose nanofibers for improving the physical and mechanical properties of papers in the paper-making industries have been evaluated and studied [15, 16]. Among other characteristics of cellulose nanofibers are their bio-compatibility, their availability and also their low price [17, 18], thus today, they are brought into much attention for being used in many different fields. So also the beneficial use of this nanofiber (BCN), for improving the physical characteristics of paper works is predictable.

Cellulose Nanofibers provide many different characteristics because of their high variety [9]. Nanofibers have been drawn into attention in some academic researches [13-19]; among which Bacterial Cellulose Nanofiber (BCN) is more famous; the results of which show the possible access to the proper characteristics of this nanofiber. BCN is made by bottom-up method and microbial culture (biosynthesis) with bacterial micro-organisms (such as Acetobacter xylinum), and thus has a high purity and numerous crystal areas [20].

Resizing method is one of the best known methods for treatment of paper works [21, 22] and it has been used by some proper polymers. Thus the use of cellulose-ethers is widely considered among paper works conservators [23]. These polymer materials, regarding their chemical qualities undergo structural changes (as yellowing) as a result of aging conditions [24], but these materials are still commonly and widely used for treatment of paper works. This research studies the physical characteristics of BCN nanofiber as a new coating on the paper works by using this nanofiber in combination with cellulose hydroxy-propyl cellulose-ether matrix (HPC) or Klucel (G type) in the form of a polymeric bio-nanocomposite.

Materials and Methods

Materials

After preparing BCN cellulose nanofiber as suspension having a specific concentration (Fig. 1A) and then determining the percentage of each one's dry matter, composited them within Klucel-G (dissolved in ethanol). The materials used here include: a) Bacterial Cellulose Nanofiber (BCN) with above 99% purity (α-cellulose content), concentration of 1%, 37nm diameter and the length of 2μm considered (Fig. 1B) as Nano-filler; b) Hydroxy-Propyl Cellulose (HPC), cellulose-ether polymer with the commercial name of Klucel-G as polymeric matrix; c) Pure cellulose filter papers (MN type) as paper samples (on behalf of paper works).

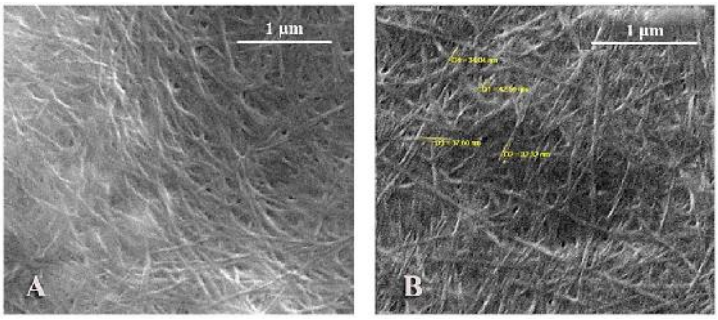

Fig. 1. Early observations by SEM images on dried film of BCN cellulose:
A. Status of without Klucel matrix; B. Cellulose Nanofibers with the average fiber diameter of 37nm

In the first step for making composites, Klucel-G powder was dissolved in ethyl alcohol (ethanol) so that the prepared solution had the composition of 1.5% w/v (weight/volume) for BCN. In the next step, suspension of BCN Nanofiber having the concentration of 2wt% was added into the prepared solution of Klucel-G polymer through hydrosoluble casting method (Fig. 2).

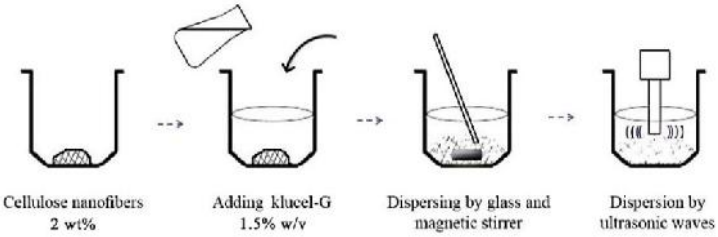

Fig. 2. A general scheme representing preparation procedure of BCN/Klucel-G nanocomposites by hydrosoluble casting method

Prior to be coated onto the sample papers, composite solutions were exposed to ultrasound waves by an ultrasonic probe (Topsonic model) for about 10 minutes under the frequency of 20kHz and the power of 200kW at 25±5°C in order to be well dispersed. Finally, dispersed composite solutions were coated onto the pure cellulose filter papers using a coater machine (K-Control coater model), at the speed of 2m/min and with the thickness of 100µm. simultaneously, polymeric films were also prepared from the composite solutions (Fig. 3) and were dried at the room temperature (25±2°C) for 24 hours. Each sample was also named by a specific code (Table 1).

Table 1. Introducing the codes of the main samples used in this study

	Samples code	Description of treatment
1.	Ref-Af1	Uncoated paper (aging 14 days)
2.	Ref-Af2	Uncoated paper (aging 24 days)
3.	Klu1.5-Be	%1.5 Klucel-G (before aging)
4.	Klu1.5-Af1	%1.5 Klucel-G (aging 14 days)
5.	Klu1.5-Af2	%1.5 Klucel-G (aging 24 days)
6.	BCN2-Be	%2 BCN + Klu1.5 (before aging)
7.	BCN2-Af1	%2 BCN + Klu1.5 (aging 14 days)
8.	BCN2-Af2	%2 BCN + Klu1.5 (aging 24 days)

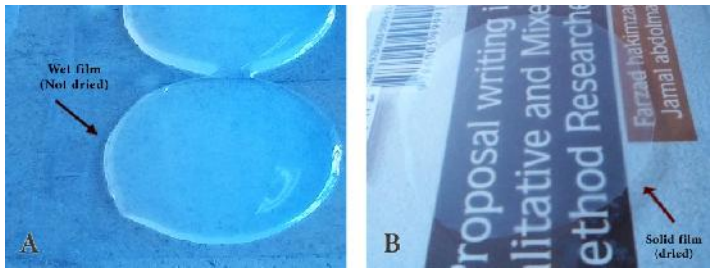

Fig. 3. A) Preparing Nanocomposite films containing BCN/Klucel-G and observation of their transparency status. A) Wet film immediately after dispersing. B) Solid or dried film after evaporation of solvent in room temperature

Methods

Accelerated Aging

Evaluation of the long-term effects of physical characteristics and behaviors about BCN nanocomposite films and coatings on the paper samples and also comparing them with their

before aging conditions is necessary. To perform the test, aging environment is organized based on TAPPI T544 SP-03 standard [25], with relative humidity of 50±5% and temperature of 90±2°C, in the two times of 14 days (336 hours) and 24 days (576 hours) aging.

Differential Scanning Calorimetry (DSC)

The purpose of this test is to study the thermal behavior (determining T_g temperature) of BCN nanocomposite films. Thus, we used a DSC1-STAR^e system model device from Mettler Toledo Company in Swiss for carrying out this test. After preparing 12 film samples based on ASTM E1356-08.5±3mg of each sample was analyzed [26]. The thermal scanning speed was organized to be 10°C/min with thermal range of 20-200ºC (in the Hot-stage).

Reflective Spectrophotometry Test (UV-Vis)

Color change behavior of paper works and especially in their aging conditions is of great importance [9, 27-33]. Therefore, Colorimetric of sample papers containing BCN nanocomposite are done by a reflective spectrophotometer device, with the visible wavelengths range of 400-700nm (model Color-Eye 7000 A: made by Gretag Macbeth Co. in America). The test was repeated for three times for each sample paper, and then, the rate of color changes of paper samples, were evaluated in the form of CIElab parameter with color spaces of L^* (brightness), a^* (red-green) and b^* (yellow-blue), based on the following experimental equations:

$$\Delta L^* = L^*_2 - L^*_1$$
$$\Delta a^* = a^*_2 - a^*_1$$
$$\Delta b^* = b^*_2 - b^*_1$$
$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

In these equations, L^*_1, a^*_1 and b^*_1 demonstrate samples without aging and 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.

Scanning Electron Microscope (SEM)

Morphologic study and microscopic observations of sample papers having BCN Nano-composite coatings and also their prepared films were done by Electron Microscope device (VEGA3, TESCAN Co. Czech Republic).

Results and Discussions

Evaluating thermal behavior (T_g) by DSC Test

Results the thermal behavior (T_g) of BCN cellulose nanofiber composite film are presented in the table 2.

Table 2. The results of DSC test, determining T_g temperature of polymeric films

	Samples code	Glass transition
1.	Klu1.5-Be	70.15
2.	Klu1.5-Af1	54.68
3.	Klu1.5-Af2	54.34
4.	BCN2-Be	72.45
5.	BCN2-Af1	65.88
6.	BCN2-Af2	61.17

The gained data from provided thermo-grams from these sample films (Fig. 4) and the study of their T_g temperature rates diagram show that the presence of these Nanofibers, would increase somewhat the glass transfer temperature for Klucel-G polymer in the form of composite (Fig. 5). Moreover, in aging condition results in the more resistance (durability) against decrease of composites' T_g compared to the matrices of Klucel (without additives).

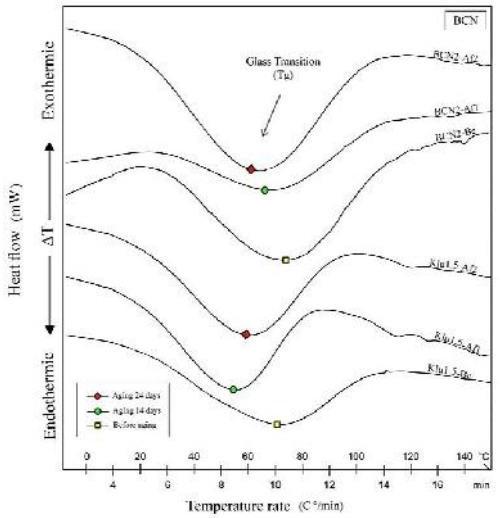

Fig. 4. Examining the results of T_g changes of polymeric films based on DSC Thermo-grams

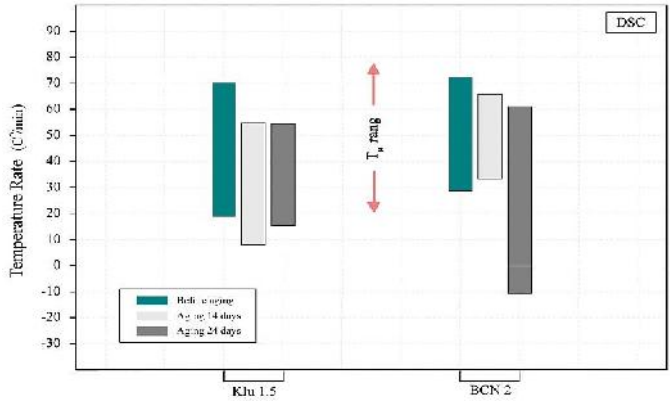

Fig. 5. Ccomparing T_g temperature changes for polymeric films based on bar-chart

It could be concluded that adding cellulose nanofibers in Klucel-G matrices, the low mobility of polymeric chains in the matrix (Fig. 6), due to the placement of these nanoparticles in the space between the polymeric chains of this matrix (in accordance with the theory of free volume), as a result, T_g temperature would increase for this polymeric matrix [34].

In addition, the other reason for increase the rate of T_g temperature for BCN can be due to the high crystalline areas in BCN structure [19, 20] since the plurality of crystal areas rather than the amorphous ones leads to the increase of polymeric matrices T_g temperature. The increase of T_g temperature about pure Klucel polymer (without additives) is related to the segment and free movements of polymeric chains (free volume), and also the increase of T_g temperature in aging conditions is due to the physical aging of polymeric chains and hence blocking the mobility of Klucel-G polymeric chains [24]. Therefore, the increase in concentration of Klucel can be effective in the increase in T_g temperature.

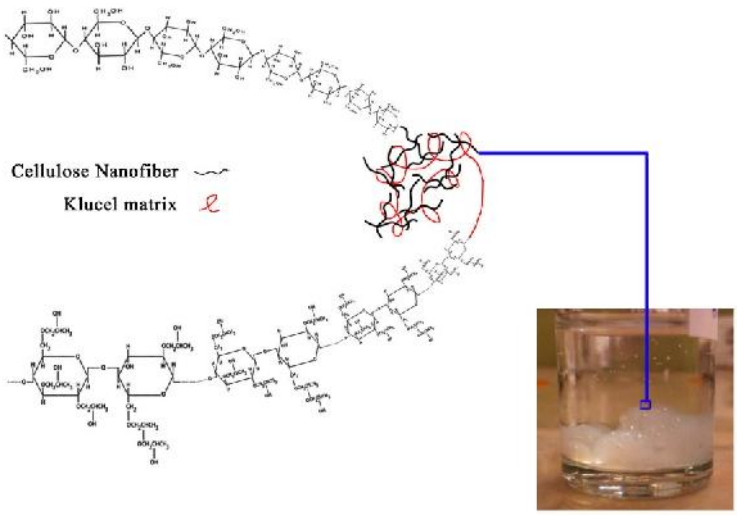

Fig. 6. Scheme of the combined status of BCN within Klucel matrix before dispersing process and also introducing chemical structure of this Nanocomposite

Evaluating color changes by UV-Vis Test

The data about color changes of sample papers are reported in tables 3 and 4. Based on the diagrams in figures 7 and 8, results show that adding BCN (before aging) in Klucel-G matrix, it would lead somewhat to the improvement of color conditions of sample papers as coatings (Lighting rate), and also in the aging conditions specifically showed the resistance against color change with the presence of this nanofiber (Prevention of color changing due to damaging effects). Besides, it was found that the higher concentration of Klucel-G in aging condition would also increase color change, but the results show a higher resistance as compared to reference papers instead (uncoated papers).

Table 3. Results of color change of sample papers according to CIELab parameters

Sample code		b^*		a^*		L^*	
		b^*_2	b^*_1	a^*_2	a^*_1	L^*_2	L^*_1
1.	Ref-Af1	7.29	3.31	-0.68	-0.59	92.47	93.73
2.	Ref-Af2	8.55	3.31	-0.69	-0.59	91.79	93.73
3.	Klu1.5-Af1	7.85	3.99	-0.41	-0.57	91.39	92.74
4.	Klu1.5-Af2	10.13	3.99	-0.61	-0.57	91.40	92.74
5.	BCN2-Af1	5.97	3.32	-0.64	-0.58	92.83	93.23
6.	BCN2-Af2	6.63	3.32	-0.70	-0.58	92.62	93.23

Table 4. Total color changes differences of papers according to CIELab parameters

Sample code		Δb^*		Δa^*		ΔL^*		ΔE
		14 days	24 days	14 days	24 days	14 days	24 days	
1.	Ref-Af1	3.98	-	-0.09	-	-1.26	-	4.17
2.	Ref-Af2	-	5.24	-	-0.10	-	-1.94	5.58
3.	Klu1.5-Af1	3.86	-	0.16	-	-1.35	-	4.09
4.	Klu1.5-Af2	-	6.14	-	-0.04	-	-1.34	6.28
5.	BCN2-Af1	2.65	-	-0.06	-	-0.40	-	2.67
6.	BCN2-Af2	-	3.31	-	-0.12	-	-0.61	3.36

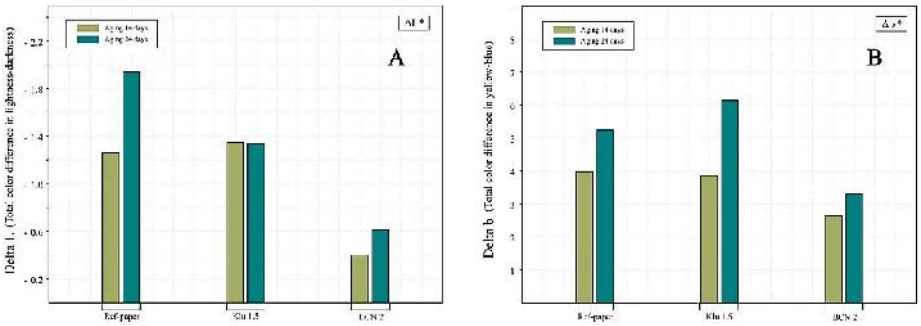

Fig. 7. Comparing rates of color changes of papers according to color space of CIELab:
A. Color changes in brightness rate; B .Changes rate in range of yellow-blue.

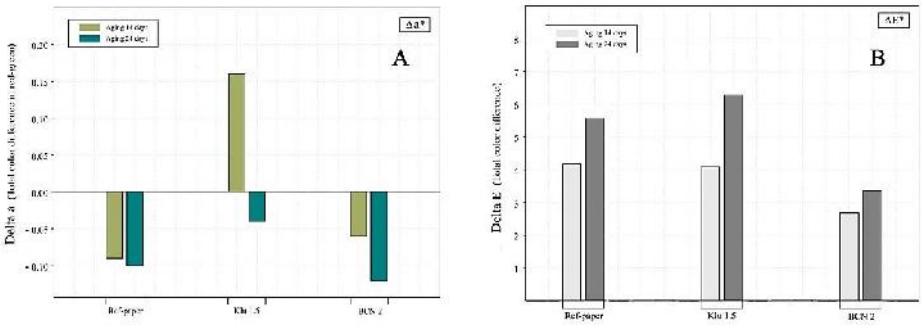

Fig. 8. Comparing rates of color change of papers according to color space of CIELab,
A. Changes rate in range of red-green; B. Total color changes.

According to these results it could be concluded that the rate of purity, degree of crystallinity and plurality of alpha cellulose in BCN chemical structure [19, 20] would lead to resistance the color changes due to oxidation reaction, and consequently the existence of secondary color compounds (Called as chromophore). Color changes of sample papers coated with Klu 1.5 matrix (without any additive), as a consequence of the depolymerization (break the cellulose polymeric chains) and thermal oxidation Klucel-G cellulosic chains [24]. and the formation of secondary products and finally the presence of colored chromophores due to the polymeric chains oxidation. Besides, the color changes of the reference papers (uncoated) are another result of the chemical degradation or oxidation of anhydroglucose units of cellulose molecules and thus the presence of more secondary groups of their colored chromophores [35-37].

Microscopic observations by SEM

Based on the SEM images, presence of BCN Nanofibers onto paper samples is approved (Fig. 9A and B) and also created coating on the surface of sample as a thin layer was approximately uniformly coated the paper surfaces.

There are some cracks into the solid film that it's because of contraction of wet film during the drying (fig. 9B) and this event can be related to low hydrogen connections of OH groups together that caused by existence of high crystallinity structure and alpha cellulose in BCN chemical structure [19-18].

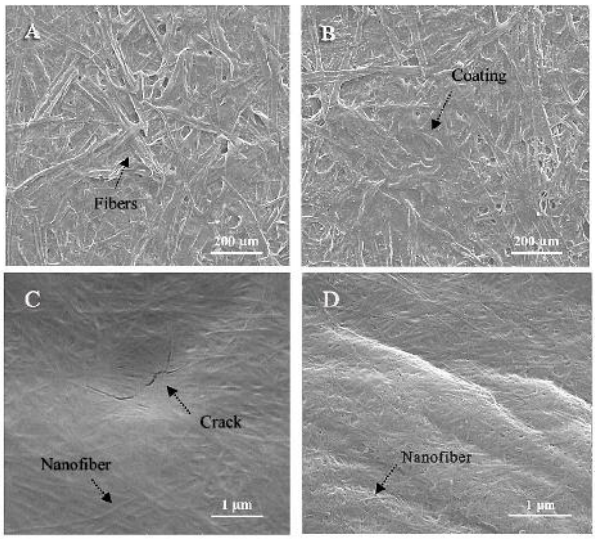

Fig. 9. SEM micrographs from paper and solid film samples containing BCN/Klucel Nanocomposite: A. Main paper without coating; B. Surface of the paper having coating; C. Dried film of BCN/Klucel; D. Textured surface of a coated fiber.

Conclusions

Findings of this study show that the specific physical characteristics of BCN cellulose Nanofiber is applicable as a protective coating in order to treatment and preservation of paper works. Results of the test of thermal behavior (T_g temperature) on solid films made from this nanocomposite demonstrated that the presence of BCN Nano-additives into Klucel-G polymer matrix would result in increasing glass temperature (T_g) in nanocomposite form, and this is accompanied by the increase of durability (resistance against the decrease of T_g temperature) in aging conditions. Results of the evaluating color change behavior of BCN nanocomposite coatings show that the presence of this nanofibers as additive into Klucel-G polymeric matrix, before aging condition would result in improvement of papers colors, and also in the aging condition, it would lead specifically to the increase of resistance against color changes when used as a coating for paper. In sum, using BCN/Klucel-G Nanocomposite as a bio-compatible, cost-effective and protective coating on the paper works could compete with pure Klucel-G polymer that in commonly used and well-known among conservators.

It is necessary to mention that this practical instruction is only provided as compared with Klucel-G polymer that its use as a very common ether-cellulose polymer in restoring paper works by conservators. Thus, in order to generalize this fact for other polymers (matrix), carrying out some new research is recommended. However, the present study has been done as a novel research with an original approach to use of cellulose nanofibers in treatment of paper works.

Acknowledgments

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