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MECHANICAL PROPERTIES OF BACTERIAL CELLULOSE NANOFIBERS BIO-COMPOSITE AS A LONG-LASTING COATING ON THE PAPER WORKS

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Abstract

One of the most important issues for treatment of paper works is use of long-lasting (endurable) materials. In this study, Mechanical properties of Bacterial cellulose Nanofibers (BCN) for preservation of paper works are investigated. For this purpose, Suspension of BCN in Klucel-G polymeric matrix with doses of 0.5, 1, and 2 Wt% of dry matter were prepared and were coated on the pure cellulose paper (filter paper) by hydro-soluble casting method, and then tensile strength (TS) and folding endurance (FE) mechanical tests were performed. Also, in order to evaluate durability properties (long-lasting) of the cellulose fiber bio-nanocomposite, accelerated aging test was conducted in moist heat conditions. After performing mechanical test, obtained results were investigated and it was observed that the presence of this nanofibers in Klucel-G matrix, although lowers the initial mechanical properties (before aging), but increases durability of bio-nanocomposite compared to pure Klucel-G polymer matrix, and hence, as protective coatings, results in prevention of early aging. As a result, this prepared nanocomposite would have applications as a new reinforcing and endurable polymeric coating for preservation of paper works and prevention from further loss of their strength, and also there would be less need for retreatment.

***Keywords**: Preservation; Paper; Cellulose nanofiber; Mechanical characteristic; Endurable coating*

Introduction

Paper works, due to their organic nature are constantly threated by various damaging agents (such as temperature, humidity, and light), which oxidize and hydrolyze the paper structure and hence lower their mechanical strength. So, conservators treat these damages and inhibit their growth utilizing a vast variety of protective materials and different reinforcing techniques. Among them, several developed approaches can be named including: silking method [1], Parylene method in plasma atmosphere [2], paper splitting [3], and some other scientific researches performed for reinforcing paper works [4, 5]. Also, wide application of conventional and common methods such as resizing by polymer adhesives (e.g. cellulose ether adhesives), lining by tissue or Japanese papers [6, 7] can be mentioned. In preservation of paper works, both durability and inertness of materials are of prime importance [8]. Sometimes deterioration and degradation of materials on the paper work may function as catalyst for decomposition, and hence, may lead to the higher speed of damaging. Thereupon, application of suitable and endurable materials for reinforcing of paper works have always been a very

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important consideration for conservators, and therefore many researchers have been focused their studies in this field. Exploitation of nanotechnology for preservation of cultural heritage with several years of experiments has endowed researchers with significant accomplishments among which preservation of paper work have received much attention. Including application of Calcium Hydroxide ($Ca(OH)_2$) nanoparticles for de-acidification [9, 10], de-acidification by Magnesium Hydroxide ($Mg(OH)_2$) nanoparticles [11], improvement of light resistant features and antibacterial properties by Titanium dioxide (TiO_2) [12], and also using a mixture of two polymers (CMC/MC) with calcium hydroxide nanoparticles for enhancement of mechanical properties of paper works [13], etc.

In this research, the applicability of mechanical properties of bacterial cellulose nanofibers (BCN) is evaluated to be used in nanocomposite as protective coatings for paper works. The previous scientific studies show that cellulose nanofibers provided polymeric Nanocomposite with desirable mechanical properties. Specific physical and mechanical features of cellulose nanofibers have been evaluated and confirmed by researchers who are specialized in other science fields (such as polymer and paper industry), and numerous articles have been published in this field [14-19]. Also, another well-known and important feature of cellulose nanofibers is their biocompatibility with surrounding environment and with nature [20, 21], which guarantees health being of conservators. Additionally, their same chemical characteristics and hence compatible nature with the environment and also similar chemical composition with substrate materials (i.e. paper works) make them to be much reliable. And this is while inertness, compatibility, and durability of materials used for treatment are of prime importance in the field of reinforcing of paper works [8, 22]. The present study investigates mechanical properties of BCN containing nanocomposite coatings. BCN nanofibers was produced through bottom-up method by bacterial biosynthesis (microbial culture) with a non-pathogenic bacteria such as Acetobacter xylinum [23-25]. Presence of multiple crystalline regions into the BCN chemical structure leads to high porosity and hence low tensile strength [26].

Introducing the cellulose nanofibers as reinforcing agents in polymer matrices and preparation of nanocomposite is a relatively new research field. The first approach in this regard, purposed about 20 years ago, was the use of cellulose micro and Nano-whisker as additives in polymeric nanocomposite (latex) [16, 17], and thereafter use of cellulose nanoparticle were commonly used as additives in various polymeric matrices. The purpose of these approaches was to reinforce and enhance physical properties of polymers so that to become more suitable to serve as protective coatings. Thus, BCN nanofibers was added to Klucel-G matrix and attempts have been made to evaluate the properties of prepared protective coatings to be used for paper works and develop an innovative advanced approach to improve conventional preservation method (resizing with Klucel-G which is commonly used in preservation of paper works).

Experimental part

Materials

BCN cellulose nanofiber suspension (having the average particle dimensions of 37nm diameter and 2µm lentgh) with the concentration of 1 wt% (bought from Nano Novin Co., Iran) (Fig. 1) were prepared in a solution of Klucel-G cellulose ether in ethanol (Lasco Co.) via hydrosoluble casting method [15]. Klucel-G is favorably micissible and compatible with cellulose nanofibers owing to its same cellulosic chemical structure. Solid content of cellulose nanofiberes suspensions was determined from the below equation:

$$Dw - (Dw + Dm) = Dm \qquad (1)$$

where: Dw is the weight of empty dish and Dm is the weight of dry matter.

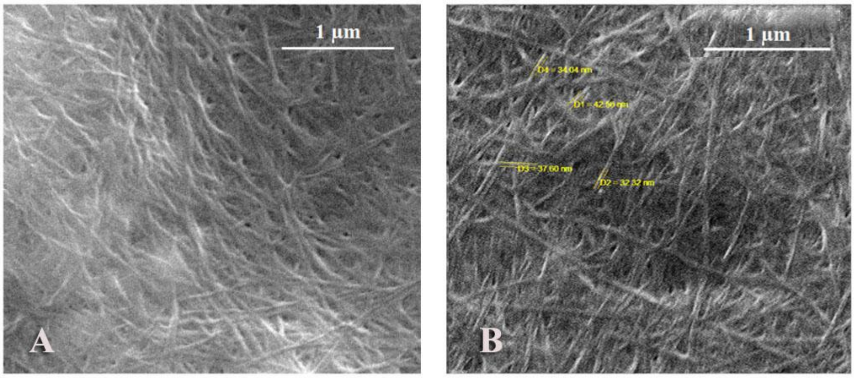

Fig. 1. Early observations by SEM images on dried film of BCN cellulose:
A. Status of without Klucel matrix; B. Cellulose Nanofibers with the average fiber diameter of 37nm

Concentrations of Klucel-G polymeric matrix in ethanol was intended to be 1.5% weight/volume for BCN. suspension of Nanofibers homogenously dispersed by the aid of an ultrasonic prob (Topsonic model) at the sonication power of 200 KW at the frequency of 20KHz for about 10 minutes at 25±5°C (Fig. 2); and then, was added into the prepared matrix at three weight percentages of 0.5, 1.0 and 2.0 wt%.

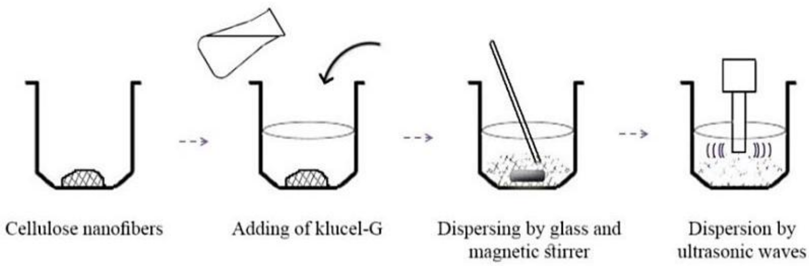

Fig. 2. A general scheme representing preparation procedure of cellulose fiber nanocomposites by hydrosoluble casting method

Pure cellulos filter papers (MN brand) were used as the substrate to be coated by prepared nanocomposite. Formation of nanocomposite films onto the paper samples with thickness of 100µm was conducted by a coater machine (K-Control coater model) at the speed of 2m/min, in order to obtain a uniform thickness of coating layer. Finally, once coating was completed, all treated samples were dried at room temperature, and an specific code was assigned to each sample (Table 1).

Table 1. Introducing the codes assigned to samples evaluated in this paper

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

Methods

Accelerated Aging

In order to evaluate the quality and and long-term effects of nanocomposite coatings on paper works, aging environment was designed to be moist heat having the relative humidity of 50±5% and the temperature of 90±2°C [27] for two time periods of 14 days (336 hours) and 24 days (576 hours) in the oven chamber.

Tensile Strength Test (TS)

After aging at moist heat, several coated samples (MN filter papers) were cut into the 15×90 mm strips for test. Uniaxial tensile test was conducted on a universal testing machine (STM-1 model) with the loadcell capacity of 20km. The gauge lenght and cross head speed were adjusted at 50±2mm and 7mm min^{-1}, respectively, at room temperature [28]. The below experimental equation was used for convertion of tensile resistance values having the unit of N to those having the unit of N/m:

$$\sigma^{b}T = F_{T}/b \quad (2)$$

where, $\sigma^{b}T$ is tensile strength in N/m unit, F_T is the average of tensile force in N unit, and b is the width of sample in mm unit.

Folding Endurance (FE) Test

Several number of samples were cut into 15×140 mm strips for folding endurance test (Fig. 3). The M.I.T testing machine (TINIUS OLSEN: 24A4BEPM-3F) having the capacity of 20-175 folding per minute was utilized. Testing condition were adjusted under the constant longitudinal load of 1kg (9.81N) and double-fold speed of 175±10 per minutes at the folding angle of 135°±2 at room temperature (25±2°C) [29].

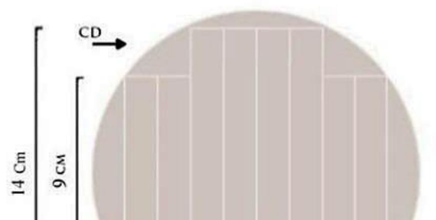

Fig. 3. Selecting direction of samples cutting, according to paper's long grain (Machine Direction or MD) and short grain (Cross Direction or CD)

Scanning Electron Microscopy (SEM)

In order to have microscopic observations and investigate the morphological features of samples, scanning electron microscope (VEGA3 TESCAN) was used.

Results and Discussions

Evaluation of Tensile Strength (TS)

The results obtained from tensile test of BCN based nanocomposite coated samples are listed in Table 2. The foundings show that increasing the concentration of Klucel-G matrix enhances tensile strength of samples in pre-aging conditions. However, this feature is far more decreased by increasing the aging time periods as compared with the case in which cellulose nanofibers are added into the polymer matrix.

Table 2. Tensile strength (TS) results of paper samples listed in N and N/m

	Samples code	TS (N)	TS (N/m)
1.	Ref-Be	51.03	3.40
2.	Ref-Af1	49.03	3.26
3.	Ref-Af2	46.49	3.09
4.	Klu1.5-Be	67.58	4.50
5.	Klu1.5-Af1	62.32	4.15
6.	Klu1.5-Af2	56.11	3.74
7.	BCN0.5-Be	61.26	4.08
8.	BCN0.5-Af1	59.23	3.94
9.	BCN0.5-Af2	56.47	3.76
10.	BCN1-Be	54.76	3.65
11.	BCN1-Af1	52.98	3.53
12.	BCN1-Af2	50.71	3.38
13.	BCN2-Be	52.69	3.51
14.	BCN2-Af1	51.56	3.43
15	BCN2-Af2	49.50	3.30

On the other hand, increasing the concentration of cellulose nano-additives in pre-aging condition although decreases tensile strength of nanocomposite samples compared to the pristine Klucel-G sample (Fig. 4), lead to an increased resistance to loweing tensile strength after the aging process (Fig. 5). Generally, the presence of cellulose nanofibers into Klucel-G polymeric matrix, despite lowering the primary tensile strength of the polymer (befor aging), leads to an increased durablity of their mechanical properties during aging, and hence prevents from deteroration of mechanical properties quality of nanocomposite coatings in aging conditions.

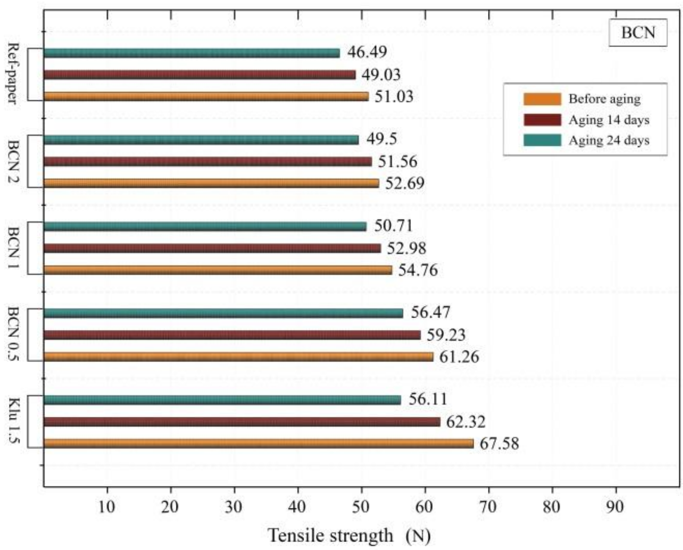

Fig. 4. Comparison of TS results between paper samples coated by BCN-based by bar chart

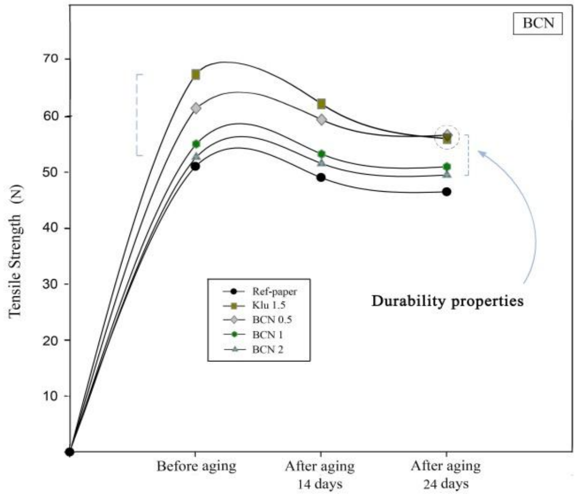

Fig. 5. Comparison the relations between TS values and aging time periods for paper samples coated by BCN-based nanocomposites

These foundings were obtained while it was expected to observe an increased tensile strength due to the presence of numerous OH functional groups as well as high aspect ratio (surface area to volume ratio) of cellulose nanofibers added as reinforcing additives in the Klucel-G polymer matrix [14-21]. Loading further content, more than 0.1%, of cellulose nanofibers in polymer matrices results in decreased mechanical strength of the matrix due to the aggregation and agglomeration of nanofibers [18] and hence their inhomogeneous distribution throughout the polymer matrix. As a consequence, irregular distrubution of mechanical stresses will be generated in the coatings leading to a decreased mechanical strength of polymer matrix.

Favorable durability of properties of prepared cellulose fiber containing coatings could be attributed to the increased physical entanglement and also increased interfacial interactions (bonding points) between cellulose nanofibers arising from their nano-scale dimensions. This phenomenon decreases physical contact of coating with environment, and finally, generates prevention behavior for these nanocomposites.

Evaluation of Folding Endurance (FE)

In this test, folding endurance of paper samples was investigated and evaluated (Table 3).

Table 3. Introducing the codes assigned to samples studied in this paper

	Samples code	Double fold
1.	Ref-Be	12
2.	Ref-Af1	6
3.	Ref-Af2	4
4.	Klu1.5-Be	21
5.	Klu1.5-Af1	9
6.	Klu1.5-Af2	6
7.	BCN0.5-Be	16
8.	BCN0.5-Af1	10
9.	BCN0.5-Af2	6
10.	BCN1-Be	14
11.	BCN1-Af1	11
12.	BCN1-Af2	9
13.	BCN2-Be	14
14.	BCN2-Af1	12
15.	BCN2-Af2	11

The foundings obtained from this test were similar to those obtained from tensile test, wich by increasing the concentration of cellulose nanofibers in Klucel-G matrix, the folding endurance of paper samples was decreased (Fig. 6). Durability of properties in aging condition, however, was increased in the presence of cellulose nanofibers (Fig. 7), and such increased durability is in direct relation with concentration of this Nano-additive.

Incresing the concentration of Klucel-G matrix (without any additive) in the aging condition results in decreased folding endurance as compared with the case in which cellulose fiber nano additives are added.

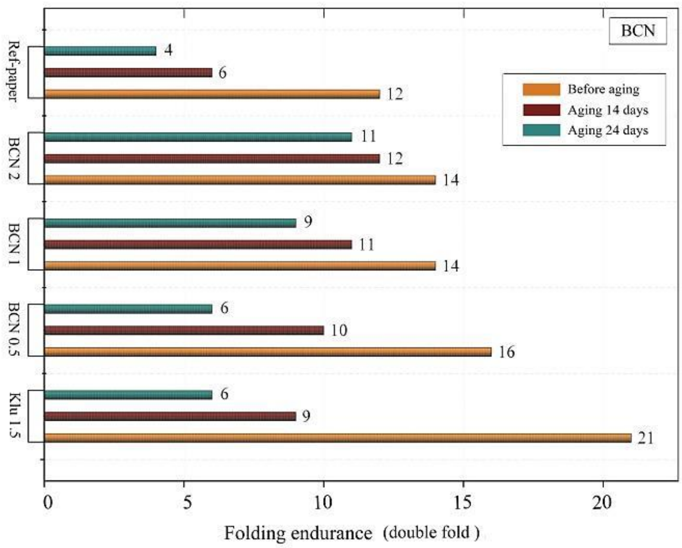

Fig. 6. Comparison between FE resultes of paper samples coated by BCN-based by bar chart

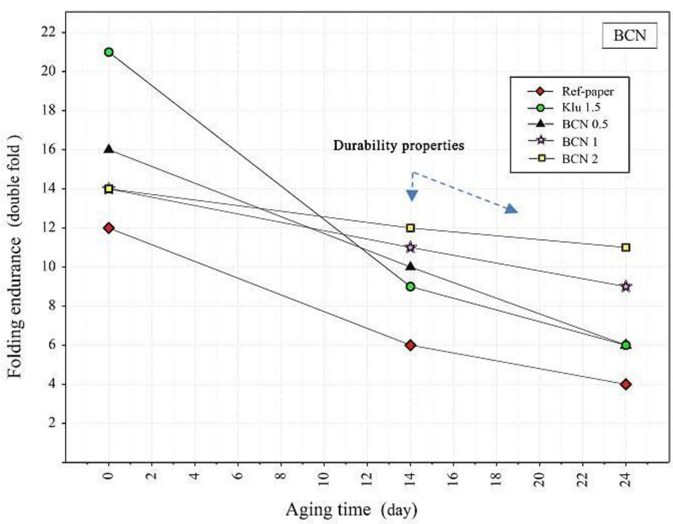

Fig. 7. Comparison of relations between FE and aging time period for paper samples coated by BCN-based nanocompisite

As it is kwoned, in generally, the presence of cellulose nanofibers into Klucel-G polymeric matrix, despite lowering the primary tensile strength of the polymer (befor aging), leads to an increased durablity of their mechanical properties during aging, and hence prevents from deteroration of mechanical properties quality of nanocomposite coatings in aging conditions (Fig. 8). Also, as it is kwoned, this feature is far more decreased by increasing the aging time periods as compared with the case in which cellulose nanofibers are added into the polymer matrix (Fig. 8A), and such increased durability is in direct relation with concentration of this Nano-additive (Fig. 8B).

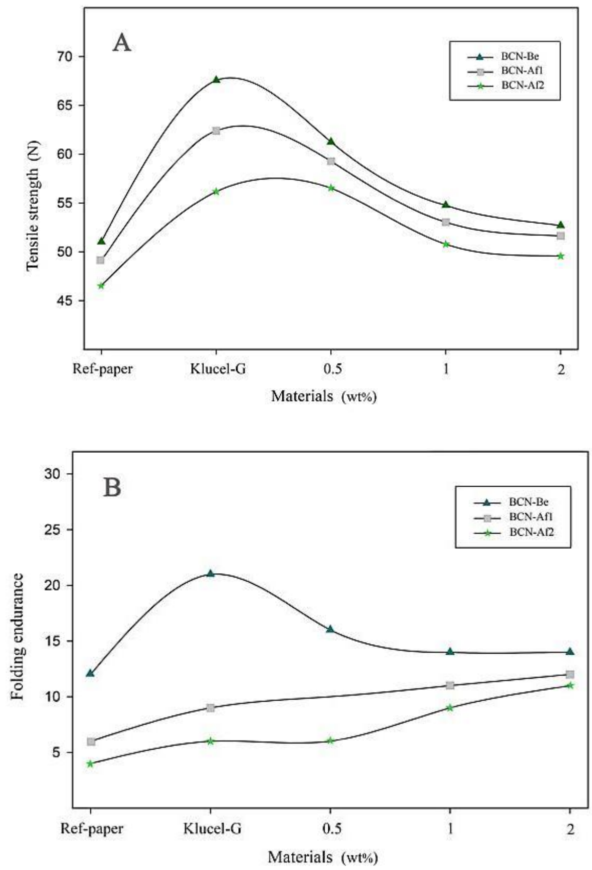

Fig. 8. Comparison between BCN's concentrations as nanoadditive into Klucel matrix and rate of changes in its mechanical behavior, before and after aging; A. TS; B. FE

It is worthy to mention that foundings obtained from this test make the enhancement conditions in far more suitable state compared to the results obtained from tensile test. On the other hand, it was observed that once BCN nanofibers are added in Klucel-G matrix, by prolonging the aging time period, folding endurance was almost maintained at higher concentration of BCN. In fact, BCN-containing nanocomposite exhibited a fairly well durability. Such higher mobility of BCN nanofibers is caused due to the formation of lower physical bonds. Folding endurance characteristics of BCN-based samples are maintained maybe for the same reason to which tensile strength characteristics was related, i.e. lower interface for exposure of coating to environment caused by the nano-scale dimensions.

Microscopic observations by SEM

Based on the SEM images, presence of BCN Nanofibers onto paper samples is approved (Fig. 9). In these images, the conditions before (Fig. 9A) and after coating (Fig. 9B) are showed. Also, as shown in images of Figure 9C and D, the coating properly has established a physical connection whit the fiber surfaces.

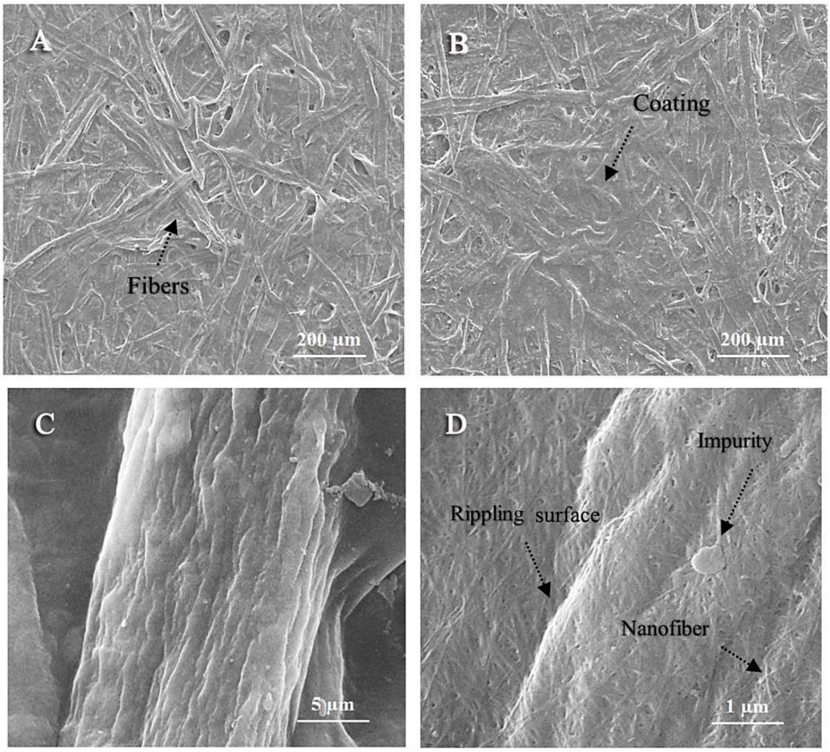

Fig. 9. SEM micrographs of papers coated by BCN-based nanocomposites:
A. Main paper without coating; B. paper surface having 2% BCN-based coating;
C. A fiber of paper coated by 2% BCN-based coating;
D. surface of a fiber coated by 2% BCN-based coating

Reversibility

The amount of reversibility of materials have always been of the great importance [8]. Owing to their similar chemical characteristic and compatible nature with the surrounding environment and with the substrate materials, cellulose nanofibers are able to minimize the degradation probability as well as serious damage to paper works. Nevertheless, the following procedure is followed for making this coating reversible. Paper samples were immersing and subsequently washed by a mixture of 1:3 water ethanol solution (one part water with 3 parts ethanol) for 5 minutes. Thus, dissolution of this coating will be possible for Klucel-G polymeric and this cellulose-based composites resulting from reversibility of Klucel films in alcohol solvents [12] and to some extent in water [30].

Conclusion

Reinforcing paper works is one of the most important factors for their preservation. Utilization of endurable and resistant materials for this purpose is of prime importance. The results obtained in the present study shows that nanocomposite coatings prepared by adding Bacterial cellulose nanofibers in Klusel-G polymer matrix exhibited increased durability of mechanical properties as well as resistance to aging process; but on the other hand, showed decreased initial properties compared to those of pure Klucel-G matrix. however, paper works having the medium strength can be treated and protected by these nanocomposite coatings. Also, this composite coating limit the need of re-treatments for paper works.

Results indicate that BCN nanocomposite coatings show more improved properties once samples are exposed to folding stresses. In sum, application condition of this nano-biocomposite coating is mainly focoused on their preventive function as endurable and protective coatings for paper works. For other preservation conditions to be studied, complementary researches must be performed. Regarding to the type of accomplishments gained in the present study, attentions will be directed toward achieving more effective mechanical properties of this cellulose nanofiber as a new method for reinforcment of paper works.

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