CELLULOSE NANOFIBER/SHELLAC NANOCOMPOSITE FILMS AS COATINGS FOR PACKAGING PAPER

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This study evaluates the efficiency of nanocomposite films prepared from cellulose nanofibers (CNF) isolated from rice straw and different ratios of shellac in terms of film properties, in addition to using a CNF/shellac mixture for coating paper sheets. The CNF/shellac nanocomposite films were prepared by the casting procedure. The weight percentage of shellac in the composition of the nanocomposite films was varied from 0 to 40%. Scanning electron microscopy was used to show the films' morphological structure. Also, the films' air permeability, tensile strength and water vapour permeability (WVP) were investigated. The outcomes showed that adding shellac to CNF can improve the films' tensile strength, WVP and air permeability characteristics. The formulation chosen for coating paper contained 60% CNF and 40% shellac. Tests were done to assess the tensile and burst strength, water absorption, air permeability and water vapour permeability of coated paper sheets. SEM analysis was performed on the surface and cross-section of coated paper sheets. It was noticed that paper sheets coated with a 90-µm thick film of CNF or CNF/shellac presented enhanced tensile strength, as well as lower water absorption, air permeability and WVP, while the burst strength properties were not affected. The addition of shellac to the composite coating produced coated paper sheets with better tensile strength compared to those of paper sheets coated with CNF alone, making them a viable choice for packaging materials.

Keywords: rice straw, cellulose nanofibers (CNF), shellac nanocomposite, paper coating

INTRODUCTION

A known natural polymer – shellac – is made from the pure resinous secretion of lac insects. It is commercially cultivated by growing such insects on host trees in Thailand and India.[1,2] Shellac is a mixture of soft and hard resins composed of single esters and polyesters, which contains carboxyl and hydroxyl groups.[3] It works well as a film-forming agent and has high barrier properties. Moreover, it is soluble in alcohol or alkali solution.[4] Shellac has a wide range of applications in the food industry. It is also used in the agro-industry to preserve products from lipid, water, gas, and microbiological deterioration, hence increasing their shelf life.[5] It is employed in the pharmaceutical industry to protect medications from moisture, being used in controlled drug delivery systems and enteric coatings for pharmaceuticals.[6] Unfortunately, shellac also has some disadvantages. Edible shellac sheets exhibit poor mechanical properties and brittleness. Native shellac films often have lower puncture resistance and elongation, compared to other natural polymers. There have been some reports on how adding plasticizers to shellac improved its mechanical properties, by creating hydrolyzed and salt-formed shellac.[7] However, this method can improve only the flexibility of shellac, but not its strength.

Composite development is an effective technique to overcome the disadvantages of natural polymers by combining them with other polymers. Thus, composite films of blended polymers are likely to have better barrier and mechanical properties. Natural and synthetic polymers, proteins and lipids can all be combined to create a variety of natural polymer mixes.[9] The compatibility between the blended polymers and their characteristics strongly affect the composite properties.[10] Hence, the shortcomings of shellac films might be reduced by mixing shellac with other hydrophilic polymers, for example, hydroxypropyl methylcellulose (HPMC) and methylcellulose (MC).[11] To overcome the poor solubility and mechanical properties, shellac was upgraded by chemical modification,[12,13] and by the addition of certain plasticizers.[13–15] Also, it has been reported that the mechanical properties of shellac composites were significantly improved by blending it with cellulose.[16]

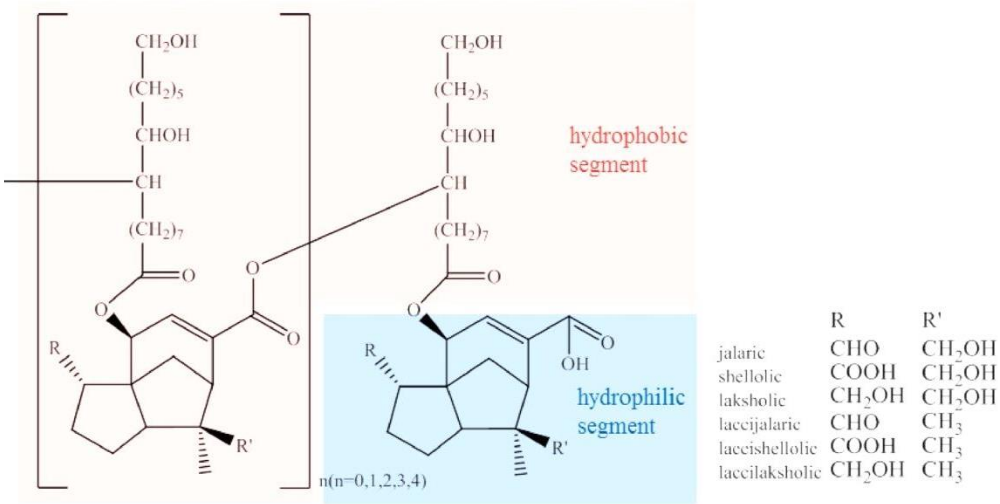


Figure 1: Amphiphilic molecular structure of shellac[8] (with agreement from Elsevier, copyright 2022)

Cellulose and shellac are both abundant natural polymers. Lately, nanomaterials based on shellac and cellulose have attracted the scientists' attention in different areas of research. Cellulose nanofibers (CNF) are a remarkable type of nanomaterial, with exceptional characteristics, such as low density, high tensile strength, transparency, oxygen barrier characteristics, chemical adaptability, and biocompatibility and biodegradability. A variety of technologies have been reported for separating CNFs from various resources; these techniques depend on the chemical-mechanical, enzymatic-mechanical, or mechanical processes used for obtaining the cellulose fibres.[17–20] The capability of CNFs to form films with good oxygen and air barrier, mechanical properties, and transparency is an additional benefit, without the need for cellulose precipitation and dissolution in order to produce the films.[21] CNFs have been used in various applications as strengthening components for nanocomposites, in drug delivery systems, tissue engineering, and coating for paper products.[22–24]

Unfortunately, cellulose is prone to microbial attack, as it has no functional groups with antimicrobial activity. In contrast, shellac has unique antimicrobial activity. Thus, considering their properties, cellulose and shellac could be blended to achieve antimicrobial composites. A suitable solvent might be used to dissolve shellac, after which it could be combined with cellulose or its solution, cast, and dried. In a previous study, such a composite was reported based on shellac blended with modified cellulose.[25] Nevertheless, to the best of our knowledge, using shellac with CNF for preparing antimicrobial films has not been studied so far.

Paper is a very suitable material for a variety of packaging applications. It may be used to make bags, milk cartons, folding cartons and sacks, among other items. It is made using sustainable natural resources and offers a number of appealing features, including recyclability, mechanical qualities, flexibility, affordability, and strong profitability. Various functional paper based materials have been investigated for meeting specific packaging requirements. For example, fire retardant paper sheets as packaging material have been prepared after different treatments, such as the treatment with modified cyclodiphosphazane.[26,27] Nanobiocomposite films from cellulose nanocrystal/polylactic acid (CNCs/PLA) were prepared with enhanced barrier, mechanical properties and structural morphology, by adding sodium lauryl sulfate (SLS) and hexadecyltrimethylammonium bromide (CTAB) as anionic and cationic surfactants, respectively, to avoid the re-aggregation of the CNCs in the PLA.[28]

The packaging is intended to shield the food from physical, chemical, and biological dangers, thus, it is crucial to the quality and safety of the food throughout its shelf life.[29] There has been a significant rise in the demand for safe, fresh, minimally processed, and ready-to-eat foods, most of which are packaged in single-use plastic packaging, which has had a negative impact on the environment.[29-32] Therefore, the development of novel biodegradable packaging materials has been the focus of innovations in the food packaging business in recent years, although overcoming their inadequate mechanical and barrier properties is still a challendge.[33,34]

In the literature, many research efforts to develop specific coatings for paper and paperboard packaging have been documented in order to improve barrier properties. For example, a hybrid of wheat gluten and silica,[35] or biodegradable starch-based polyelectrolyte complexes were used with outstanding barrier efficacy in paper and paperboard packaging.[36,37] Moreover, biodegradable chitosan/polyvinyl alcohol functionalized with catechol displayed high UV barrier capabilities, with considerable potential in the field of active packaging.[38,39]

The present study aimed to prepare CNF/shellac composites and use them as coatings for paper sheets, in order to investigate their potential for packaging applications. The properties of the CNF/shellac nanocomposite films, in terms of their WVP, water swelling, tensile strength and air permeability, were studied. Furthermore, the influence of the CNF/shellac nanocomposite coating on the WVP, air permeability and tensile strength properties of the paper sheets was analysed.

EXPERIMENTAL

Materials

Rice straw was pulped for two hours at 150 °C in a 15% aqueous sodium hydroxide solution to produce rice straw pulp. The pulp was bleached using a solution of sodium chlorite and acetic acid, after being washed with water to achieve a pH balance.[40] According to established procedures, the chemical composition of the bleached pulp was as follows: holocellulose 69.7%, hemicelluloses 19.7%, Klason lignin 1.46%, and ash content 10.6%.[41] Commercial-grade shellac was used according to the manufacturer's specifications. Other chemicals used were analytical-grade and were used as received.

Preparation and characterization of cellulose nanofibers (CNF)

In accordance with earlier published methods, bleached rice straw pulp was used to obtain cellulose nanofibers (CNF).[42] TEMPO (0.048 g, 0.3 mmol), sodium bromide, and 3 g of bleached rice straw pulp were combined in 400 mL of distilled water (0.48 g, 4.8 mmol). The pH of the suspension was then brought down to 10 with 0.1 N sodium hydroxide solution after 30 mL of sodium hypochlorite solution (4%) was added while stirring. By the end of the reaction, 0.1 HCl solution was used to bring the pH level down to 7. The oxidized pulp was centrifuged at 5000 rpm, before being further cleaned through repeated cycles of dispersion in water and centrifugation. The dialyzation of the oxidized pulp against deionized water was the last step.

A high-shear homogenizer (CAT Unidrive 1000), operating at 10,000 rpm, disintegrated the acquired CNF into a suspension of 2% oxidized pulp in water. The produced CNF had 0.31 mmol/g of carboxylic groups, as measured using the TAPPI Test Method T237 cm-98. Moreover, high-resolution transmission electron microscopy was used to characterize the CNF (JEM-2100 Transmission Electron Microscope, JEOL, Japan).

Preparation and characterization of CNF and CNF/shellac films

Films made from CNF and CNF/shellac aqueous suspensions (solid content, 2%) were cast on Teflon Petri plates and dried at 40 °C for 12 hours in an oven with circulating air. The formulations contained glycerol, which was added as a plasticizer in a weight ratio of 25%, and shellac in ratios ranging from 0 to 40 weight percent, based on the dry weight of CNF and glycerol.

The films were then pressed for 5 minutes at 100 Pa and 105 °C. The films underwent a 48-hour conditioning at 50% relative humidity before being tested. A Lloyd instrument (Lloyd Instruments, West Sussex, United Kingdom), with a 100-N load cell, was used to assess the tensile strength properties of the films at 25 °C. Strips of 1 cm wide by 8 cm long were used for the tests, the crosshead speed was 2 mm/min. Each sample was measured five times, and the average was calculated. A Bendtsen smoothness and air permeability tester (Denmark, Model 5, No. 11772) was used to perform the air permeability tests. Also, the films were subjected to static WVP testing in accordance with ASTM standard E96-95 (ASTM Standards, 1995).

Coating of paper sheets with CNF and CNF/shellac films

Bleached rice straw pulp (60%) was combined with bleached bagasse pulp (20%) and bleached wood pulp (20%) to prepare paper sheets with a basic weight of 80 g/m^2. The pulp blend was then beaten to 40° SR. Paper sheets were coated manually using a coating bar, with variable gap clearance, with CNF or CNF/shellac (60:40) aqueous suspension (solid content ~2%). Then, paper sheets coated with different coating thicknesses (30, 60, 90, 120 µm) were achieved by using an Elcometer 3520 Baker Film Applicator, Belgium. The coated paper sheets were dried in air and then pressed at 100 Pa, 107 °C for 5 min.

The microstructure of coated paper sheets was observed using an FEI Quanta 200 Scanning Electron Microscope (FEI Company BV, Netherlands), at an acceleration voltage of 20 kV. The TAPPI T494-06 standard procedure was used to conduct the tensile strength tests. A constant crosshead speed of 2 mm/min was used on a universal testing machine (LR10K, Lloyd Instruments, Fareham, UK), equipped with a 1 KN load cell. The span was 10 cm, and paper strips of 20 cm long by 15 mm wide were utilized. The burst strength of both untreated and treated specimens was tested in accordance with ISO 2758.

Paper sheets were tested for water absorption using the Cobb method, in accordance with ISO 535. Paper sheets were tested for water vapour permeability (WVP) using the ASTM standard (ASTM E96).

RESULTS AND DISCUSSION

Preparation and characterization of CNF/shellac composite films

This work mainly aimed to use TEMPO-oxidized cellulose, which has a negative charge,[43] in combination with shellac. CNF and shellac composites were prepared based on CNF loaded with different ratios of shellac. Shellac is an amphiphilic biomacromolecule, with a distinctive molecular construction, consisting of cyclic terpene acids and aleuritic acid, as revealed in Figure 1. The cyclic terpene acids and aleuritic acid are connected with ester bonds, acting, respectively, as the hydrophilic and hydrophobic constituents[8] of shellac. Films from CNF and CNF/shellac were formed by the casting method using glycerol as plasticizer. The shellac to CNF weight ratio ranged from 0 to 40%; the formed films were homogeneous, without any signs of shellac particles aggregation, as observed by the naked eye.

The flexibility of the films was proper, as noted from fast-bending trials. The flexibility of composites is an important feature if the composites are intended to be used in packaging applications. The film thickness was different due to the presence of shellac. The thickness of the neat CNF film was 0.06 mm, while the thickness of the films incorporating 5, 10, 20, 30 and 40% of shellac was 0.08, 0.09, 0.13, and 0.16 mm, respectively.

Surface morphology of films

The microstructure of the prepared CNF/shellac nanocomposite and CNF film was examined. The SEM image of the CNF film shows a smooth surface, as can be seen in Figure 2a. After blending with shellac, the surface the CNF/shellac nanocomposite film became darker, with aggregation of the nanofibers into larger bundles (Fig. 2b, c).

Air permeability of CNF and the impact of shellac

The films' air permeability was investigated and the effect of shellac addition on the films' air permeability is shown in Table 1. It is clear from the data that the addition of shellac to the CNF had an excellent effect on the air permeability of the films, as shellac and CNF formed homogenous films and no air permeability was remarked for any of the investigated CNF/shellac nanocomposite films. This may be a consequence of good adhesion between CNF and shellac, as can be judged by the smooth surface of the films, as shown in SEM images. This indicates that the addition of shellac made the film structure more compact, *i.e.*, with very low air permanence, compared to the film based on CNF alone. This outcome is in agreement with other publications.[44,45] Also, the results are in agreement with those reported earlier for shellac film composites, where a good oxygen barrier could be obtained, due to low air permanence (about 0.001 nm/Pa).[46] This indicates that the nanocomposite films resulted from blending CNF and shellac present a good barrier property and could be used in packaging applications.[25]

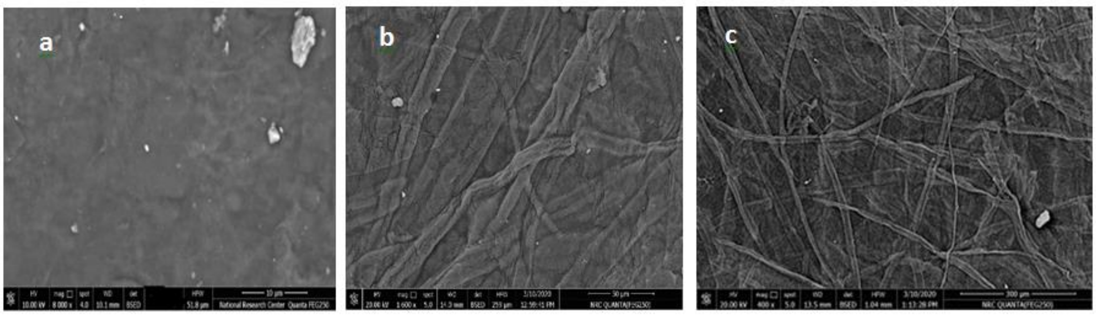


Figure 2: Scanning electron micrographs (SEM) of CNF and shellac nanocomposite films; (a) CNF, (b) 5% shellac and 95% CNF, (c) 40% shellac and 60% CNF

Table 1
Properties of CNF/shellac nanocomposite films

Shellac, wt%	Tensile strength (MPa)	Elastic modulus (MPa)	Strain at max. load (%)	Air permeability (s/100 mL)
0	16.92 (6.15)	557.3 (29.96)	14.2 (1.7)	462
5	53.33 (2.79)	948.59 (213.51)	8.96 (2.61)	Nil
10	59.42 (8.50)	525.47 (32.29)	26.53 (3.38)	Nil
20	68.11 (21.21)	783.39 (79.21)	18.74 (5.18)	Nil
30	68.88 (5.53)	1760.66 (113.81)	6.10 (1.61)	Nil
40	73.00 (0.76)	2796.88 (94.60)	3.50 (0.64)	Nil

*Values in brackets are the standard deviation

Effect of shellac on mechanical properties of CNF

The influence of adding shellac on the properties of the resulted CNF films was considered and reported in Table 1. In this investigation, the mechanical characteristics that were measured were strain at maximum load, elastic modulus, and tensile strength. According to the results obtained, the elastic modulus and tensile strength of the CNF films were both improved by the addition of shellac. Increasing the shellac content in the CNF films increased their tensile strength by about 215% to 331%, with a maximum at 40% shellac loading, as compared to the neat film. Also, increasing the shellac ratio in the CNF film caused an increase in the elastic modulus – with an increment from 70.3% to 402% upon raising the loading of shellac from 5 to 40%. These results may be attributed to the existence of shellac between the CNF fibrils, which increased the bonding between the CNF fibrils in the areas close to the shellac, and to the stronger interaction between the CNF and shellac. As revealed before, the presence of shellac in CNF films caused an increase in cohesive strength.[47] Regarding the strain at maximum load, the addition of 10% of shellac to the CNF film had an optimum value. Higher amounts of shellac in the formulation had a negative effect on the strain at maximum load, thus, the maximum loading of 40% shellac resulted in a decrease in the strain by about 41–75%, as shown in Table 1. The nanocomposite films presented superior flexibility, thus, they could be bent without cracking. The thickness of the films increased with the loading of shellac, as follows: the neat CNF film had a thickness of 0.06 mm, while the thickness of the films with 5, 10, 20, 30 and 40% of shellac was 0.08, 0.09, 0.13, and 0.16 mm, respectively.

It should be pointed out here that the reinforcing effect of shellac depends on different factors, the most critical being the uniform dispersion of the reinforcing material in the matrix of the composite.[48] Due to the amphiphilic property of shellac, *i.e.*, presence of both hydrophilic (carboxylic and hydroxyl groups) and hydrophobic (long alkane chains) moieties in its structure, it can be dispersed in both aqueous and non-aqueous media. However, to increase the stability of the shellac dispersion in composites, the addition of plasticizers, such as glycerol, is of help – it stabilizes the dispersion of shellac in an aqueous formulation or in the presence of hydrophilic polymer matrices like cellulose.[49] The use of some nanoparticles can also improve the dispersion of shellac in composite films.[50] The CNF used in the current work also has good dispersion properties in water and it may be assumed that it can stabilize the dispersion of other amphiphilic materials and solid nanoparticles within its network structure.[51] In fact, the interface of shellac/CNF also contributes to the reinforcing effect of shellac and the improvement in the properties of the nanocomposite films in general. The surface of the TEMPO-oxidized CNF used in the present study is rich in hydrophilic carboxylic groups; this makes the CNF compatible with the hydrophilic part of shellac, which contains carboxylic groups too. The negative charge on both of CNF and shellac carboxylic groups could result in good dispersion in water and also good homogeneity (insignificant agglomeration) upon film formation.

Water vapor permeability of CNF/shellac nanocomposite films

The effect of adding different ratios of shellac on the WVP of CNF films was considered and the results are presented in Figure 3. It was discovered that, although the CNF has a tight surface structure, water vapours can pass through it. This might be due to the texture of the film and the potent hydrophilic nature of the CNF. The absorbed moisture by -OH and -COOH groups within the cellulosic fibrils has a significant impact on the permeability of water vapour within cellulose. In the current work, the addition of shellac to CNF resulted in improving the water vapour resistance for all the films, as the WVP values of the film decreased, compared to that of the neat CNF, as revealed in Figure 3. Actually, the data in Figure 3 reveal that the WVP was very little impacted by the increase in shellac ratio. Still, it was observed that 30% shellac was the optimum ratio, in terms of WVP values, in comparison with both the film with neat CNF and the films with other ratios of shellac used in this study.

When compared to other natural polymers, the lower WVP of the shellac film is what makes it distinctive.[4,52] It is known that the WVP is reliant on the hydrophilicity or solubility of the film's elements. Generally, the WVP is increased when the constituents have higher hydrophilicity or aqueous solubility.[6] Actually, within a hydrophilic film similar to CNF, the WVP is based on both absorption of water molecules and diffusivity in the film matrix.[53] Otherwise, the presence of particles or molecules such as shellac within the formulation decreases the spaces among the fibers, also leading to partial closure of film surface nano-pores, which promotes lower water vapor diffusivity within the composite film. This could explain the improved WVP of the composite films, compared to the neat CNF one.

Evaluation of paper sheets coated with CNF and CNF/shellac

In this investigation, paper sheets were coated with CNF/shellac nanocomposite films in order to assess their impact on the characteristics of the resulting coated sheets. The paper sheets were coated with the CNF/shellac mixture that contained 40% shellac. The neat CNF and CNF/shellac films that were produced had various thicknesses – of 30, 60, 90, and 120 microns. The mechanical characteristics, water absorption, and air and water vapour permeability of coated paper sheets were examined, and the results are shown in Table 2 and Figure 4. According to the table, coating paper sheets with CNF only and with CNF combined with shellac increased the breaking length of the paper sheets substantially, especially in cross direction (CD). Moreover, the thickness of the films, in the case of both CNF and CNF/shellac, had a pronounced effect on the breaking length of the paper sheets.

The improvement in the breaking length of paper sheets coated with CNF/shellac was higher compared to that in the case of the paper coated by CNF only for a film thickness of 30 microns. The greater tensile strength of the CNF/shellac film, compared to that of CNF may be the cause of the higher breaking length of the sheets coated with it, compared to those coated with CNF.[54] These results agreed with the findings of previous studies.[55,56] The burst strength of the resulting coated paper sheets, however, was slightly reduced after coating them with CNF or CNF/shellac films. As a result, the sheets covered with CNF and CNF/shellac had nearly identical burst strengths. The decline in the burst strength could be explained by paper composition as well as by other factors.[57,58]

In this study, the water absorption on the coated side of the paper sheets was measured using the Cobb test method. The results showed that the coating reduced the water absorption of the sheets by about 22%, in the case of the sample coated with the CNF film of 90 m thickness. This may be explained by the CNF layer's decreased porosity, in comparison with that of uncoated paper, which causes water to penetrate more slowly.

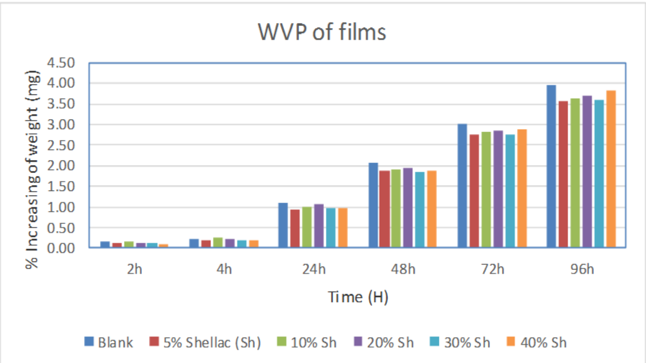


Figure 3: Water vapor permeability of different CNF and CNF/shellac films

Table 2
Physical and mechanical properties of paper sheets coated with CNF/shellac

Formulation	Breaking length (m) CD	Breaking length (m) MD	Burst strength (kg/cm^2)	Water absorption (WA), (g/m^2)	% WA change	Air permeability (AP), (s/100 mL)	% AP change
Paper sheet (P)	1484.9 (240.7)	3979.6 (355.7)	1.175	118.9	0.00	229	00
P+30 CNF	1875.4 (76.2)	4021.2 (256.1)	1.075	114.0	4.10	239	4.37
P+60 CNF	1749.6 (91.7)	3507.1 (682.6)	1.15	108.56	8.71	446	94.76
P+90 CNF	1818.2 (46.4)	3832.7 (38.0)	1.15	93.29	21.55	427	86.46
P+120 CNF	1620.2 (108.7)	3900.9 (419.5)	1.075	97.13	18.33	453	97.82
P+30 CNF/ Shellac	1922.6 (89.9)	4147.0 (77.9)	1.1	84.73	28.75	308	34.50
P+60 CNF/ Shellac	1674.6 (188.5)	4083.4 (131.5)	1.075	55.46	53.37	433	89.08
P+90 CNF/ Shellac	1807.2 (20.8)	3919.3 (264.4)	1.1	49.19	58.63	620	170.7
P+120 NF /Shellac	1608.2 (87.4)	3932.2 (161.6)	1.075	78.02	34.39	650	183.8

*Values in brackets are the standard deviation

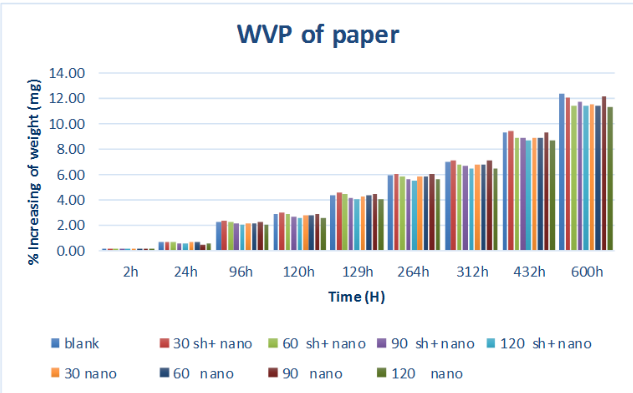
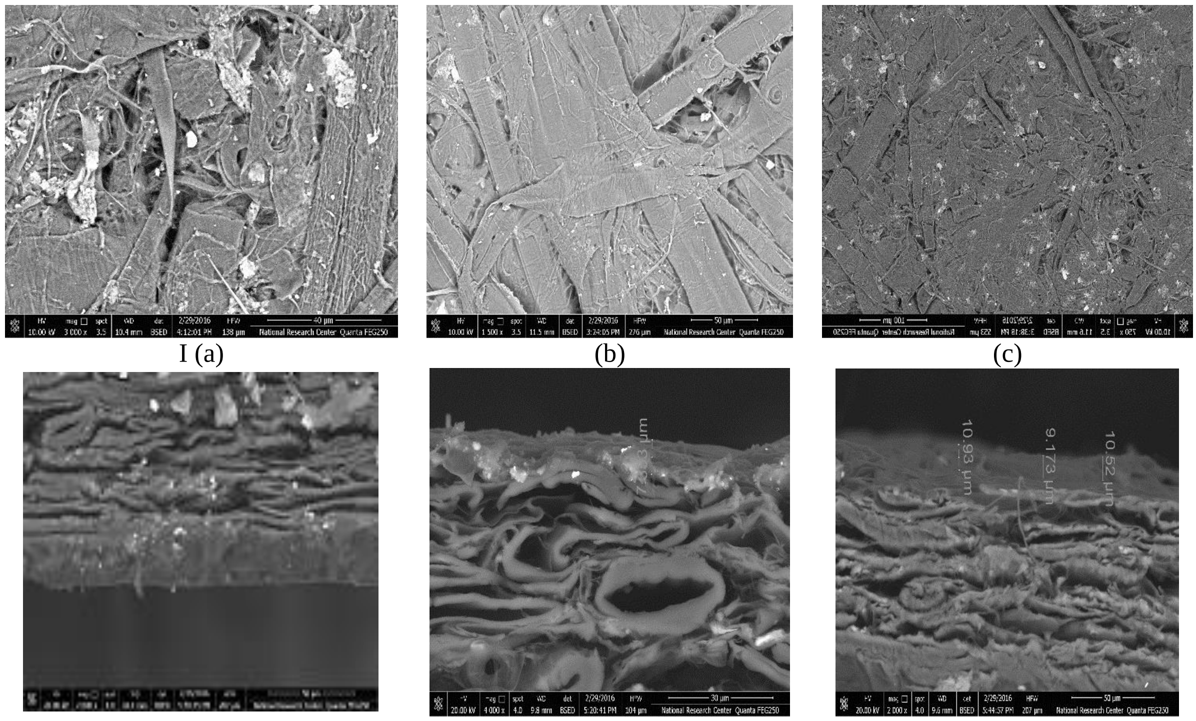


Figure 4: Water vapour permeability of papers coated with CNF and CNF/shellac films of various thicknesses

When shellac is added to CNF and applied as a coating mixture, it significantly reduces the water absorption values of the sheets, with a reduction in water absorption of roughly 59%, compared to the blank uncoated paper sheets. This may be explained by the fact that the addition of shellac makes the paper more hydrophobic compared to the paper sheet coated with CNF only.[14]

From Table 2, it can be noticed that both shellac and CNF films can improve the air barrier properties of paper sheets and the improvement was increased by increasing the thickness of the coating on the paper sheets. The increase in air permeability ranged from 4.4% to 98% with increasing the CNF film thickness from 30 µm to 120 µm, and from 34.4% to 184% with increasing the CNF/shellac film thickness from 30 µm to 120 µm. The enhancement in air permeability was more pronounced in the case of the composite film, compared to the neat CNF. The better barrier properties of the CNF/shellac coating may be attributed to the higher efficiency of shellac particles in closing the surface pores of the paper.[25]

Figure 4 shows the impact of CNF and CNF/shellac coatings on the water vapour permeability (WVP) of paper sheets. This graphic illustrates that the WVP was enhanced when the surface of the paper sheets was covered with the coatings. Also, it can be seen that the WVP values were significantly affected by the thickness of the film utilized in this investigation. As may be noted, the WVP value was lower for the paper sheets coated with the composite film, compared to those coated with the neat CNF, the film thickness of 120 microns yielding the best results for both types of coatings. Due to strong hydrophilicity of CNF and its nanoporous structure, the paper sheets coated with it have higher WVP values than those coated with CNF/shellac. Also, it seems that the presence of shellac in the composite film offers more efficient closure of surface nano-pores on the CNF layer.[25]



I (a) (b) (c)

II (a) (b) (c)

Figure 5: SEM images of surfaces (I) and edges (II) of paper sheets (a) uncoated, (b) coated with 30 CNF, and (c) coated with 30 CNF/shellac

SEM of paper sheets coated with CNF/shellac nanocomposite films

Figure 5 shows the surface morphology of the paper sheets coated with CNF and CNF/shellac coatings. The coating thickness selected in this test was 30 microns, considered as the optimum based on the results for the physical and mechanical properties of coated paper sheets. SEM images reveal that, after coating with the prepared CNF and CNF/shellac formulations, excellent film formation had occurred. The composite coatings covered well the surface of the paper and in-between the surface fibres. SEM images of the cross-section of the paper sheets coated with the CNF/40% shellac film showed no visual difference compared to that coated with CNF only. The images also reveal that shellac was homogenously distributed, without agglomeration, as may be seen especially in cross-section images, where the thickness of CNF/shellac film was around 24 µm, while CNF film thickness was about 12.7 µm. On the other hand, there was no discernible variation in the surface pore size of the CNF and CNF/shellac coated samples.

Thus, cellulose nanofibers (CNF) based materials can be a viable solution for achieving ecologically friendly packaging. Using alternative lignocellulosic sources, such as agricultural residues, for obtaining the cellulose may be a substantial step forward in the creation of environmentally friendly materials for food packaging.[59]

CONCLUSION

New efficient CNF/shellac nanocomposite films with good homogeneity, tensile strength, and air permeability properties could be obtained. Different ratios of shellac to cellulose nanofibers were studied (0-40%). The addition of shellac to CNF improved the film properties, even at the lowest used addition percent (5%). The optimum level of shellac in the formulation was dependent on the desired property. For example, the optimum level of shellac to get the maximum increase in the mechanical properties (tensile strength and modulus) was 40%, while the optimum level of shellac for the maximum air barrier (lowest air permeability) and water vapor property was 5%. Higher levels of shellac did not show any significant changes.

Coatings based on shellac in combination with CNF imparted good WVP and air permeability paper properties, when using a 120-µm gap thickness, while the coating with 90-µm gap thickness was the optimum for the lowest water absorption. In general, coating paper sheets with CNF/shellac improved their tensile strength properties, WVP and air permeability, while reducing water absorption. The prepared coated sheets meet the food packaging requirements, where good WVP and barrier properties are essential, but they could also find application in hygienic paper products.

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REFERENCES

[1] K. P. Krause and R. H. Müller, *Int*. *J*. *Pharm*., **223**, 89 (2001), https://doi.org/10.1016/S0378-5173(01)00730-X

[2] L. Yu, K. Dean and L. Li, *Prog*. *Polym*. *Sci*., **31**, 576 (2006), https://doi.org/10.1016/j.progpolymsci.2006.03.002

[3] A. N. Singh, A. B. Upadhye, V. V Mhaskar and S. Dev, *Tetrahedron*, **30**, 867 (1974), https://doi.org/10.1016/S0040-4020(01)97149-2

[4] S. Limmatvapirat, C. Limmatvapirat, S. Puttipipatkhachorn, J. Nuntanid and M. Luangtana-Anan, *Eur*. *J*. *Pharm*. *Biopharm*., **67**, 690 (2007), https://doi.org/10.1016/j.ejpb.2007.04.008

[5] S. A. Valencia-Chamorro, M. B. Pérez-Gago, M. Á. del Río and L. Palou, *Postharvest Biol*. *Technol*., **54**, 72 (2009), https://doi.org/10.1016/j.postharvbio.2009.06.001

[6] N. Pearnchob, A. Dashevsky and R. Bodmeier, *J*. *Control*. *Release*, **94**, 313 (2004), https://doi.org/10.1016/j.jconrel.2003.10.004

[7] S. Limmatvapirat, D. Panchapornpon, C. Limmatvapirat, J. Nunthanid, M. Luangtana-Anan *et al*., *Eur*. *J*. *Pharm*. *Biopharm*., **70**, 335 (2008), https://doi.org/10.1016/j.ejpb.2008.03.002

[8] Y. Yuan, N. He and Q. Xue, *Trends Food Sci*. *Technol*., **109**, 139 (2021), https://doi.org/10.1016/j.tifs.2021.01.031

[9] H. Yai, *Int*. *Food Res*. *J*., **15**, 237 (2008), http://ifrj.upm.edu.my/15%20(3)%202008/01.%20Bourtoom,%20T.pdf

[10] M. Licchelli, M. Malagodi, M. Somaini, M. Weththimuni and C. Zanchi, *Surf*. *Eng*., **29**, 121 (2013), https://doi.org/10.1179/1743294412Y.0000000069

[11] B. Qussi and W. G. Suess, *Drug Dev*. *Ind*. *Pharm*., **32**, 403 (2006), https://doi.org/10.1080/03639040600559099

[12] S. A. Valencia-Chamorro, L. Palou, M. Á. del Río and M. B. Pérez-Gago, *LWT - Food Sci*. *Technol*., **44**, 2342 (2011), https://doi.org/10.1016/j.lwt.2011.02.014

[13] S. A. A. Mohamed, M. El-Sakhawy, E.-S. H. A. Nashy and A. M. Othman, *Int*. *J*. *Biol*. *Macromol*., **136**, 774 (2019), https://doi.org/10.1016/j.ijbiomac.2019.06.130

[14] E. A. Hassan, M. L. Hassan, R. E. Abou-Zeid and N. A. El-Wakil, *Ind*. *Crop*. *Prod*., **93**, 219 (2016), https://doi.org/10.1016/j.indcrop.2015.12.006

[15] P. Piyawatakarn, *Adv*. *Mater*. *Res*., **506**, 290 (2012), https://doi.org/10.4028/www.scientific.net/AMR.506.290

[16] B. Schad, B. Cheng, E. Van Ness, T. Riley, J. Scholten *et al*., *Pharm*. *Technol*., (2013), https://www.pharmtech.com/view/coating-and-taste-masking-shellac

[17] S. A. A. Mohamed, M. El-Sakhawy and M. A.-M. El-Sakhawy, *Carbohyd*. *Polym*., **238**, 116178 (2020), https://doi.org/10.1016/j.carbpol.2020.116178

[18] H. P. S. A. Khalil, Y. Davoudpour and M. N. Islam, *Carbohyd*. *Polym*., **99**, 649 (2014), https://doi.org/10.1016/j.carbpol.2013.08.069

[19] Y. Zhang, T. Nypelö, C. Salas, J. Arboleda, I. C. Hoeger *et al*., *J*. *Renew*. *Mater*., **1**, 195 (2013), https://doi.org/10.7569/JRM.2013.634115

[20] S. Kalia, S. Boufi, A. Celli and S. Kango, *Colloid Polym*. *Sci*., **292**, 5 (2014), https://doi.org/10.1007/s00396-013-3112-9

[21] H. Fukuzumi, T. Saito, T. Iwata, Y. Kumamoto and A. Isogai, *Biomacromolecules*, **10**, 162 (2009), https://doi.org/10.1021/bm801065u

[22] E. Hassan, S. Fadel, W. Abou-Elseoud, M. Mahmoud and M. Hassan, *Polymers* (*Basel*), **14**, 4605 (2022), https://doi.org/10.3390/polym14214605

[23] M. L. Hassan, J. Bras, E. Mauret, S. M. Fadel, E. A. Hassan *et al*., *Ind*. *Crop*. *Prod*., **64**, 9 (2015), https://doi.org/10.1016/j.indcrop.2014.11.004

[24] S. M. Fadel, W. S. Abou-Elseoud, E. A. Hassan, S. Ibrahim and M. L. Hassan, *Ind. Crop. Prod.*, **180**, 114787 (2022), https://doi.org/10.1016/j.indcrop.2022.114787
[25] E. L. Hult, M. Iotti and M. Lenes, *Cellulose*, **17**, 575 (2010), https://doi.org/10.1007/S10570-010-9408-8
[26] A. A. Younis, S. A. A. Mohamed, M. A. El-Samahy and A. H. A. Kader, *Egypt. J. Pet.*, **30**, 25 (2021), https://doi.org/10.1016/j.ejpe.2020.12.005
[27] A. A. Younis, S. A. A. Mohamed and M. El-Sakhawy, *Egypt. J. Pet.*, **30**, 29 (2021), https://doi.org/10.1016/j.ejpe.2021.10.001
[28] R. E. Abou-Zeid, M. A. Diab, S. A. A. Mohamed, A. Salama, H. A. Aljohani *et al.*, *J. Renew. Mater.*, **6**, 394 (2018), https://doi.org/10.7569/JRM.2017.634156
[29] N. Bhargava, V.S. Sharanagat, R.S. Mor, and K. Kumar, *Trends Food Sci. Technol.*, **105**, 385 (2020), https://doi.org/10.1016/j.tifs.2020.09.015
[30] M. S. Firouz, K. Mohi-Alden and M. Omid, *Food Res. Int.*, **141**, 110113 (2021), https://doi.org/10.1016/j.foodres.2021.110113
[31] S. Chakori, A. A. Aziz, C. Smith and P. Dargusch, *Ecol. Econ.*, **185**, 107063 (2021), https://doi.org/10.1016/j.ecolecon.2021.107063
[32] H. Sundqvist-Andberg and M. Åkerman, *J. Clean. Prod.*, **306**, 127111 (2021), https://doi.org/10.1016/j.jclepro.2021.127111
[33] M. Sánchez-Gutiérrez, I. Bascón-Villegas, E. Espinosa, E. Carrasco, F. Pérez-Rodríguez *et al.*, *Foods*, **10**, 1584 (2021), https://doi.org/10.3390/foods10071584
[34] L. Pinto, M. A. Bonifacio, E. De Giglio, E. Santovito, S. Cometa *et al.*, *Food Packag. Shelf Life*, **28**, 100676 (2021), https://doi.org/10.1016/j.fpsl.2021.100676
[35] C. Rovera, H. Türe, M. S. Hedenqvist and S. Farris, *Food Packag. Shelf Life*, **26**, 100561 (2020), https://doi.org/10.1016/j.fpsl.2020.100561
[36] K. Chi, H. Wang and J. M. Catchmark, *Food Hydrocoll.*, **103**, 105696 (2020), https://doi.org/10.1016/j.foodhyd.2020.105696
[37] S. Wang, D. Han, Y. Chai, K. Liu, K. Liang *et al.*, *Cellulose Chem. Technol.*, **56**, 787 (2022), https://doi.org/10.35812/CelluloseChemTechnol.2022.56.70
[38] S. A. A. Mohamed, M. El-Sakhawy and S. Kamel, *Cellulose Chem. Technol.*, **52**, 423 (2018), https://cellulosechemtechnol.ro/pdf/CCT5-6(2018)/p.423-431.pdf
[39] Y. Lei, L. Mao, J. Yao and H. Zhu, *Carbohyd. Polym.*, **264**, 117997 (2021), https://doi.org/10.1016/j.carbpol.2021.117997
[40] L. E. Wise, *Pap. Trade*, **122**, 35 (1946), https://www.semanticscholar.org/paper/A-CHLORITE-HOLOCELLULOSE%2C-ITS-FRACTIONATION-AND-ON-Wise-Murphy/53f10e1d55261efe9fe84a6d2317b4d901d95274
[41] P. Calvo, C. Remunan-Lopez, J. L. Vila-Jato and M. J. Alonso, *J. Appl. Polym. Sci.*, **63**, 125 (1997), https://doi.org/10.1002/(SICI)1097-4628(19970103)63:1<125::AID-APP13>3.0.CO;2-4
[42] T. Saito, S. Kimura, Y. Nishiyama and A. Isogai, *Biomacromolecules*, **8**, 2485 (2007), https://doi.org/10.1021/bm0703970
[43] A. Isogai, *J. Japan Pet. Inst.*, **58**, 365 (2015), https://doi.org/10.1627/jpi.58.365
[44] Q. Luo, K. Li and J. Xu, *J. Agric. Food Chem.*, **64**, 9374 (2016), https://doi.org/10.1021/acs.jafc.6b04417
[45] S. Soradech, J. Nunthanid, S. Limmatvapirat and M. Luangtana-Anan, *Food Control*, **73**, 1310 (2017), https://doi.org/10.1016/j.foodcont.2016.10.059
[46] E.-L. Hult, M. Iotti and M. Lenes, *Cellulose*, **17**, 575 (2010), https://doi.org/10.1007/s10570-010-9408-8
[47] S. Soradech, J. Nunthanid, S. Limmatvapirat and M. Luangtana-Anan, *J. Food Eng.*, **108**, 94 (2012), https://doi.org/10.1016/j.jfoodeng.2011.07.019
[48] J. Obradovic, F. Petibon and P. Fardim, *BioResources*, **12**, 1943 (2017), https://doi.org/10.15376/biores.12.1.1943-1959
[49] S. Soradech, S. Limatvapirat and M. Luangtana-Anan, *J. Food Eng.*, **116**, 572 (2013), https://doi.org/10.1016/j.jfoodeng.2012.12.035
[50] M. L. Weththimuni, C. Milanese, M. Licchelli and M. Malagodi, *Coatings*, **11**, 419 (2021), https://doi.org/10.3390/coatings11040419
[51] Y. Chu, Y. Sun, W. Wu and H. Xiao, *Carbohyd. Polym.*, **250**, 116892 (2020), https://doi.org/10.1016/j.carbpol.2020.116892
[52] N. Pearnchob, J. Siepmann and R. Bodmeier, *Drug Dev. Ind. Pharm.*, **29**, 925 (2003), https://doi.org/10.1081/DDC-120024188
[53] A. Akhgari, F. Farahmand, H. A. Garekani, F. Sadeghi and T. F. Vandamme, *Eur. J. Pharm. Sci.*, **28**, 307 (2006), https://doi.org/10.1016/j.ejps.2006.03.005
[54] N. Gontard, S. Guilbert and J. Cuq, *J. Food Sci.*, **57**, 190 (1992), https://doi.org/10.1111/j.1365-2621.1992.tb05453.x

[55] S. K. Sharma, S. K. Shukla and D. N. Vaid, *Def. Sci. J.*, **33**, 261 (1983), https://core.ac.uk/download/pdf/333721598.pdf
[56] K. Torvinen, T. Helin, H. Kiiskinen, E. Hellén, C. Hohenthal *et al*., in *Procs. TAPPI International Conference on Nanotechnology for Renewable Materials 2011*, TAPPI Press, 2011, pp. 260–270, https://imisrise.tappi.org/TAPPI/Products/11/NAN/11NANO20.aspx
[57] M. Bilodeau, D. Bousfield, W. Luu, F. Richmond and M. Paradis, in *Procs. TAPPI International Conference on Nanotechnology for Renewable Materials*, TAPPI Press, 2012, https://imisrise.tappi.org/TAPPI/Products/12/NAN/12NANO20.aspx
[58] P. Bajpai, "Biermann's Handbook of Pulp and Paper: Volume 1: Raw Material and Pulp Making", Elsevier, 2018, https://www.sciencedirect.com/book/9780128142400/biermanns-handbook-of-pulp-and-paper
[59] L. Amoroso, K. J. de France, C. I. Milz, G. Siqueira, T. Zimmermann *et al*., *ACS Sustain. Chem. Eng.*, **10**, 342 (2021), https://doi.org/10.1021/acssuschemeng.1c06345