Enhancement of water resistance and antimicrobial properties of paper sheets by coating with shellac

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ABSTRACT
The present study was focused on the effect of shellac as a natural polymer on the mechanical, physical, and antimicrobial properties of the paper sheets. The surface modification of paper sheets was carried out using different shellac solutions. The capability of the treated sheet to absorb water and to permit air flow was studied by Cobb test and air permeability, respectively. It was found that the treated sheet had little affinity for water and low air permeability. The change of sheet surface properties after modification was ascertained by scanning electron microscopy and Fourier Transform Infrared Spectrophotometer (FT-IR). The shellac treated paper sheet displayed improved mechanical properties when compared with untreated paper sheet. The shellac treated sheets exhibit efficient antimicrobial activity against Staphylococcus aureus, Pseudomonas aeruginosa, and Candida albicans. Consequently, the prepared paper sheet can be used as novel materials for packaging applications.

Keywords: Shellac; Paper sheet; Mechanical properties; Air permeability; Water Resistance; Antimicrobial activity.

1. INTRODUCTION
In the last decades commercial and technical interests in cellulose have been increased as a recyclable, renewable, biodegradable and sustainable substitute to oil products. In fact, the only renewable materials used for packaging are paper and paperboard. Nevertheless, their sensitivity to moisture limited their application. Moisture resistance is among the main reason for using of synthetic plastic in packaging materials [1]. In addition, aluminum foils and plastic polymers are usually used as a barrier film in multilayer structure combined with paperboard. But these materials are non-renewable and their recycling process is difficult. To minimize the disposal problem of food package after using, many efforts are ongoing to recognize substitute packaging materials deriving from agricultural crops [2, 3]. Natural coatings and films from lipids, proteins and polysaccharides could be used to manage the mass transfer in packaging and therefore increase food shelf life [4].

In general paper sheet is formed from network structure between cellulose, hemicelluloses, and lignin. These materials are held together with hydrogen bonds. By increasing the crossing between the cellulose fibers the mechanical properties of paper sheet can be improved [5]. A number of natural and synthetic polymers have been applied to increase the inter-fiber bonding between the cellulose chains in the formed paper sheets [6-9].

Shellac is obtained from secretions of scale insects (e.g. Kerria Lacca) which are parasitic on some indigenous trees in Asia, particularly Thailand and India. The shellac resin is not a single compound but consists of an intimate mixture of several polar and non-polar components in a molecule. It contains, as a main component, terpenic resin (70–80%) and wax (6–7%), colored substances (4–8%) and other impurities. The resin portion is a complex mixture of esters (y30%, soft resin) and polyesters (y70%, hard resin) consisting of sesquiterpenic acids and hydroxy fatty acids [10].

Shellac is a natural and versatile resinous polymer used for coating applications and it has occupied the most important position among the natural occurring resins. Its industrial applications are many. In the last centuries it has been widely used as a decorative lacquer for wooden handicrafts. It still finds application as wood sealer and finisher because of its peculiar properties [11]. Shellac is presently used for different types of applications as pharmaceutical, confectionery and food coatings. Pearnhob et al. used shellac as a moisture-protective, taste-masking coating and also to prolong release matrix tablets [12]. In fruit coating and in nutraceutical industries shellac is an approved food additive and is also has generally recognized as safe [13-14].

Natural resin shellac as an abundant, cheap and soluble in aqueous alkaline medium has been used for jute yarns by surface treatment to develop the bonding between fiber and resin at the interface of natural fiber-reinforced composites [15].

Mohamed et al. studied the antimicrobial activity of shellac, CMC and gelatin composites, novel green composites films based on CMC, gelatin and shellac was used as safe eco-friendly packaging materials. The formed films were proven as good mechanical properties and active as anti-microbial [16]. Shellac has been widely used for gas, water, lipid and microbial spoilage protection to extend the products shelf-life in agro and food industries. Shellac antimicrobial film is a promising polymer for medical products used as wound dressing [17].

Cellulose and shellac accomplish the European Union policy on materials in contact with food and they both fulfill with the American food and drug organization laws about the materials components when contact with food. Packaging composites based
on cellulose and shellac has the prospective to give the environmental advantage of recycling or composting as final disposal [18]. So, the current study focused on the production of water resistance and antimicrobial paper sheets by coating the paper sheet with shellac. Optimization of the coating was achieved by investigating different solubility conditions and different shellac concentrations.

2. EXPERIMENTAL SECTION

Materials.
The paper sheet was kindly provided by Rakta Company, Egypt (basic weight 80 g/m², made from bleached rice straw pulp (60 %) blended with bleached bagasse pulp (20 %) and bleached wood pulp (20 %)). Shellac is produced by the solvent extraction method and is commercially available; the solvent used was commercial ethanol grade chemicals and anhydrous sodium pure laboratory grade.

Methods

Preparation of alcoholic and aqueous shellac solutions. Different concentrations of shellac (0.5, 1, 3 and 5 % wt/v) were prepared by dissolving in ethanol then filtrated (clear shellac solution in ethanol) or in different concentrations of sodium carbonate solution (0.5, 1, 3 and 5 % w/v), then filtrated. Different concentrations (1, 3, 5, 7, 9 and 10 % wt/v) of shellac dissolved in ethanol without filtration (colloidal shellac solution in ethanol) were also prepared, and all of them were dissolved by stirring at room temperature.

Treatment the paper sheets by alcoholic and aqueous shellac solutions. The paper sheets were immersed in the three types of shellac solutions for 1 min. Then paper sheets were dried in air at room temperature.

Paper testing. The average thickness of the conditioned loaded paper sheets was found to be 0.234 mm. The sheets were weighed and subjected to the following tests.

Basis weight (g/m²). Basis weight is the weight in grams per square meter of paper.

\[
\text{Basis weight} = \frac{\text{weight of paper sheet in g}}{\text{Area in of paper sheet in sq.m}}
\]

Water absorption (Cobb). The water absorption of paper sheets was carried out as follows: the weighed paper sheet was put in Cobb apparatus, 100ml of water was added over the paper, left for two minutes, the water was poured. The paper sheet was dried well between two filter papers and the sheet weighed.

\[
\text{Cobb (g/m², min)} = (\text{Weight of paper after} – \text{Weight of paper before}) \times 100.
\]

Air permeability. Air permeability (always referred to as porosity) is an indispensable parameter. The air permeability test was carried out on a BENDTSEN Smoothness and Porosity Tester, Andersson and Sørensen, Copenhagen. Air permeability is the flow of air (cm²/min⁻¹) passing through 1 cm² surface of the test piece at a measuring pressure of 1.00 kPa. The air permeability units are cm²/min⁻¹ cm⁻² at 1 kPa.

Burst strength. It is defined as the pressure at which a sample of paper sheet bursts. Compressed air is applied to the paper sheet and the rate adjusted so that the paper bursts after 20 seconds. The burst strength is recorded on the pressure gauge of the tester in kg/cm². Burst strength tests were conducted according to Tappi standard T403 on a Mullen tester (Perkins, Chicopee, MA, U.S.A.).

Strength properties. Strength properties were estimated according to the Tappi Standard Methods.

Strength properties. Strength properties were carried out with Tappi Standard Methods.

Tensile strength (breaking length). Tensile strength calculates the paper resistance to direct tension. It is the necessary forces for breaking a paper strip of precise length and width. The tensile strength could be converted to breaking length which is more correct since it takes the basis weight and thickness of paper sheet into consideration. The breaking length is the paper length when the paper strip breaks under its personal weight. The breaking length in m is attained by the following correlation:

\[
\text{Breaking Length in meter} = \frac{\text{Tensile Strength}}{\text{Weight of strip}}
\]

Scanning electron microscopy. Surface morphology of control sheet and coated sheets was assessed by SEM observation using scanning electron microscopy (a Zeiss ULTRA55 Scanning Electron Microscope (SEM) with an acceleration voltage of 15 kV). Each sample was coated with gold/palladium alloy before observation.

Fourier Transform Infrared Spectrophotometer. Fourier Transform Infrared Spectrophotometer (FT-IR) spectra of paper sheets were recorded in the range of 400–4000 cm⁻¹ on (Shimadzu 8400S) FT-IR Spectrophotometer.

Assay of antibacterial activity. The disc diffusion method was used to determine the antimicrobial activity of the prepared paper sheets. A volume of 0.1 mL (=109 cells/mL), of the tested microorganisms was inoculated on Brian Heart Infusion Broth (at 42 °C for 24 h), and then spread on the entire surface of the dish using a sterile spatula. Subsequently, sterile discs were placed onto agar at certain intervals by passing gently. After the plates were incubated at 42°C for 24h, the inhibition zones around the discs were measured in millimeters, the experiments were repeated in duplicated for all of the test strains [19].

3. RESULTS SECTION

Shellac is insoluble in water, glycerol and esters but dissolves readily in alcohol, aqueous solution of alkalis, organic acids and ketones. This finding has led to the conclusion that hydroxyl, carboxyl and carbonyl groups are present in shellac.
Several problems arise during shellac treatments, especially concerning the sensitivity to alcoholic solvents and aqueous basic reagents, which may induce alteration of the physical state and cause softening and darkening of the surfaces.

FT-IR spectroscopy.
A characteristic carbonyl stretching band at 1712 cm\(^{-1}\), was used as indication of the shellac penetration in paper sheets. This band, which distinguishes the carbonyl compound presence in components, was observed for the paper modified with shellac. Figure 2a shows the most important characteristic peaks of the bagasse paper sheet, band at 3473-3365 cm\(^{-1}\) is assigned to O-H stretching and band at 2904 cm\(^{-1}\) is due to CH stretching. The band located at 1646 cm\(^{-1}\) is ascribed to twist vibration of the absorbed water molecules. The FTIR spectrum of shellac displayed peaks around 1716 cm\(^{-1}\), 1255 cm\(^{-1}\) and 3430 cm\(^{-1}\) due to the carbonyl stretching, C=O and O-H stretching, respectively [20].

The FTIR spectrum of the paper modified with clear shellac solution in ethanol (Figure 2b), displayed peaks around 1644, 1272, 2935, 3476-3369 cm\(^{-1}\), due to the carbonyl stretching, C=O, CH stretching and O-H stretching, respectively. While the paper modified with colloidal shellac solution in ethanol (Figure 2c), displayed peaks around 1712, 1276, 2939, 3457-3417 cm\(^{-1}\) due to the carbonyl stretching, C=O, CH stretching and O-H stretching, respectively. But Figure 2d, since the paper modified with solution of shellac in sodium carbonate salt (Na\(_2\)CO\(_3\)), shows absorption at 1593, 1379 cm\(^{-1}\), indicating the asymmetric and symmetric C=O stretching of carboxylate respectively, and absorption at 2904 cm\(^{-1}\), due to CH stretching. The result was in agreement with other studies [21].

Mechanical properties.
The mechanical properties of untreated and treated paper sheets were assessed by constant rate elongation method. Figure 3 and Tables 1-2 display the breaking length, tear, and burst strength as a function of shellac %.

Treatment with shellac enhanced the breaking length considerably from 3708 m for blank paper to 5114 m for paper treated with 9 % colloidal shellac solution in ethanol, Table 2. When the paper sheets treated with the solution of different concentrations of clear shellac solution in ethanol, breaking length was enhanced considerably from 3708 m for blank paper to 4394 m for paper treated with 5% shellac. Also, when the paper sheets treated with the solution of different concentrations of shellac dissolved in Na\(_2\)CO\(_3\), the breaking length values increased considerably from 3708 m for the blank paper to 4207 m\(^2\) for paper treated with 5% shellac which confirmed superior compatibility between shellac and cellulose in paper.

Tensile strength increases by treatment with shellac until it achieves a stable rate at about 18.5 % increase of tensile strength compared with untreated paper sheets. This could be elucidated by the effect of the differences in the paper sheets microstructures.

Treatment with shellac enhanced the burst strength considerably from 0.95 for blank paper to 1.33 (Kg/cm\(^2\)) for paper treated with 9 % colloidal shellac solution in ethanol. When paper sheets treated with different concentrations of clear shellac solution in ethanol, the burst strength increased considerably from 0.95 for blank paper to 1.20 (Kg/cm\(^2\)) for paper treated with 1% shellac, Table 1. Paper sheets treated with different concentrations of clear shellac solution in ethanol, the burst strength enhanced considerably from 0.95 for blank paper to 1.05 (Kg/cm\(^2\)) for paper treated with 0.5% shellac which confirmed superior compatibility between shellac and cellulose in paper. Table 2. Burst strength increases by treatment with shellac until it reaches a steady level at about 40 % increase of burst strength compared with untreated paper sheets.
sheets which confirmed superior compatibility between shellac and cellulose in paper. Different samples of paper sheets treated with shellac (dissolved in ethanol or Na₂CO₃) did not show any improvement in tear properties compared to untreated paper sheets.

Table 1. Effect of shellac % in different solvents on mechanical properties of paper sheet.

| Shellac % | Tear (g/m²) | Burst (Kg/cm²) |
|-----------|-------------|----------------|
| Ethanol   | Na₂CO₃      | Ethanol        | Na₂CO₃        |
| 0.0       | 32          | 32             | 0.95          | 0.95          |
| 0.5       | 26          | 26             | 0.95          | 1.05          |
| 1.0       | 26          | 26             | 1.20          | 0.88          |
| 3.0       | 26          | 20             | 1.00          | 0.85          |
| 5.0       | 32          | 20             | 1.15          | 0.88          |

Air permeability. Treatment with shellac enhanced air permeability considerably from 53 for blank paper to 428 sec for paper treated with 10% colloidal shellac solution in ethanol, and when the paper sheets treated with a clear ethanol solution of shellac the air permeability enhanced considerably from 53 for blank paper to 67 sec for paper treated with 3% shellac. Air permeability improved by treatment with shellac until it achieves a stable rate at about 707% decreasing of air permeability for 10% colloidal shellac solution in ethanol compared with untreated paper sheets, which established the compatibility between shellac and cellulose in paper. Presence of ester groups distributed on the paper sheet surface may be a motive for increasing tensile strength; increasing the burst strength values, and decreasing of air permeability by about 707% compared with untreated paper sheets. But paper sheets treated with shellac dissolved in Na₂CO₃ did not show any enhancement in air permeability. This could be elucidated by the effect of the differences in the paper sheets microstructures.

Table 2. Effect of colloidal shellac %, solution in commercial ethanol, on mechanical properties of paper sheet.

| Shellac % | B.L. | Tear (gm) | Burst (Kg/cm²) |
|-----------|------|-----------|----------------|
| Blank     | 3708 | 32        | 0.93           |
| Ethanol   | 3534 | 24        | 0.92           |
| 1         | 4598 | 26        | 1.05           |
| 3         | 4590 | 24        | 1.2            |
| 5         | 4655 | 22        | 1.23           |
| 7         | 5021 | 22        | 1.25           |
| 9         | 5114 | 24        | 1.33           |
| 10        | 5073 | 20        | 1.32           |

Table 3. Effect of shellac % and solvent on Air permeability (Sec/100 mL) of paper sheet.

| Shellac % | Ethanol clear solution | Ethanol colloidal solution | Na₂CO₃ |
|-----------|------------------------|----------------------------|--------|
| 0.0       | 53                     | 53                         | 53     |
| 0.5       | 43                     | 44                         | 40     |
| 1.0       | 51                     | 56                         | 42     |
| 3.0       | 67                     | 89                         | 39     |
| 5.0       | 66                     | 147                        | 39     |
| 7         | --                     | 248                        | --     |
| 9         | --                     | 380                        | --     |
| 10        | --                     | 428                        | --     |

Water resistance. Effect of shellac on water resistance of paper sheet was investigated. Treatment with shellac reduces the Cobb values considerably from 88.6 for blank paper to 43.1 g/m² for paper treated with 9% colloidal shellac solution in ethanol. When paper sheets treated with different concentrations of clear shellac solution in ethanol, Cobb values reduced considerably from 88.6 for blank paper to 36.69 g/m² for paper treated with 5% shellac. Water resistance increases by treatment with shellac until it reaches a steady level at about 51.91% decrease of water absorption compared with untreated paper sheets, which confirmed superior improvement in water resistance. This can be explained by the effect of the variations of paper sheets microstructures. After treatment by hydrophobic material (shellac) which reduced water absorption and then reduced Cobb values compared with untreated paper sheets. This could be due to ester group’s distribution on the paper sheet surface which reduced water absorption and then reduced Cobb values Table 4. All samples which treated with shellac dissolved in Na₂CO₃ did not show any resistance to water absorption.

Table 4. Effect of shellac % on water sorption (g/m²) of paper sheet.

| Shellac % | Ethanol colloidal solution | Ethanol clear solution |
|-----------|---------------------------|------------------------|
| 0         | 88.6                      | 88.6                   |
| 0.5       | --                        | 77.07                  |
| 1         | 72.98                     | 77.45                  |
| 3         | 74.16                     | 72.17                  |
| 5         | 72.68                     | 36.69                  |
| 7         | 64.79                     | --                     |
| 9         | 43.10                     | --                     |
| 10        | 53.19                     | --                     |

Scanning Electron Microscopy. Scanning electron microscopy is a most suitable tool for morphometrical studies of fibers and paper. Figure 4 shows SEM images for untreated paper sheet, paper sheet coated with 5% clear shellac solution in ethanol and paper sheet coated with 5% colloidal shellac solution in ethanol. Figure 4 (a), shows that paper sheet had a rough surface with many pores, while paper sheet coated with 5% clear shellac solution in ethanol (Fig.4 b)) had only some pores and shellac covered the cellulosic fiber. Figure 4 (c) shows that the cellulosic fibers were covered well by 5% colloidal shellac solution in ethanol (appear as dark splotches), whereas the paper sheet had a soft smooth surface with tiny pores. Thus, SEM analysis disclose a precise difference between the untreated and treated paper sheets. Figure 4 demonstrates the dispersion of shellac on the surface of the paper sheets coated with shellac in ethanol with/without filtration.

Antimicrobial activity. Antimicrobial activity was estimated by calculation of growth inhibition zone around the agent’s discs in millimeters. The shellac treated sheets exhibit efficient antimicrobial activity against Staphylococcus aureus, Pseudomonas aeruginosa, and Candida albicans, Figure 5. Mohamed et al. demonstrated that the antimicrobial activity of shellac, CMC and gelatin mixed composites. The formed films were proven active as anti-microbial and the obtained results indicated that different types of composite films have different efficiency towards microbial growth depends on the ratio of shellac [16].


Enhancement of water resistance and antimicrobial properties of paper sheets by coating with shellac

In terms of the surrounding clearing zone, the shellac film did not show inhibitory effect against all tested microorganisms. In the Gram-positive bacteria, the major constituent of its cell wall is peptidoglycan and there is very little protein. The cell wall of Gram-negative bacteria on the other hand is thinner but more complex and contains various polysaccharides, proteins and lipids beside peptidoglycan. The cell wall of Gram-negative bacteria also has an outer membrane, which constitutes the outer surface of the wall [22].

The antimicrobial effect of shellac occurred without migration of active agents. Only organisms in direct contact with the active sites of shellac are inhibited. In general, shellac film itself showed some antimicrobial effect even though it did not reveal the inhibitory zone in any microorganisms tested. This is reasonable as shellac has the innate characteristic of antimicrobial activity itself. Consequently, the prepared paper sheet could be used as materials for packaging applications.

4. CONCLUSIONS

Tensile strength increases by treatment with shellac until it achieves a stable rate at about 18.5 % increasing of tensile strength and burst strength increases by treatment with shellac until it achieves a stable rate at about 40 % increasing of burst strength compared with untreated paper sheets which confirmed superior compatibility between shellac and cellulose in paper. Air permeability decreases by treatment with shellac until it achieves a stable rate at about 707 % decreasing of air permeability compared with untreated paper sheets. Water resistance increases by treatment with shellac until it achieves a stable rate at about 51.9 % decrease of water absorption compared with untreated paper sheets. This can be explained by the effect of the variations of paper sheets microstructures after treated by hydrophobic material (shellac). The shellac treated sheets exhibit efficient antimicrobial activity. Consequently, the prepared paper sheet may be used as novel materials for packaging applications.

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6. ACKNOWLEDGEMENTS

Authors would like to express their gratitude to the National Research Centre, Egypt, for the financial support.

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