CHITOSAN AS A PAPERBOARD COATING ADDITIVE FOR USE IN HVAC (HEATING, VENTILATION AND AIR CONDITIONING) APPLICATIONS

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In this study, commercial chitosan and fungal chitosan were used to formulate solutions that were then coated onto unbleached Kraft paper, to serve as an alternative to phenolic resin coatings. This type of coated paper is used to manufacture evaporative cooling pads for use in livestock enclosures. The critical-to-quality (CTQ) parameters chosen for comparing the chitosan-based materials with the phenolic resin materials were vertical wicking and wet Taber stiffness. The fungal chitosan coating achieved a wet Taber stiffness of 13.34 milliNewtons (mN), and a vertical wicking height of 0.045 meters (1.771 in), while the commercial chitosan coating achieved a wet Taber stiffness of 14.71 mN and a vertical wicking height of 0.032 meters (1.259 in). Phenolic resin, in contrast to both chitosan coated substrates, achieved a lower wet Taber stiffness of 8.83 mN, and a vertical wicking height of 0.034 meters (1.338 in), which is comparable to the commercial coated chitosan, but is substantially lower than the fungal chitosan-coated paper. The commercial chitosan-coated sheet showed a lower mass gain due to water absorption than phenolic resin-coated sheets. This indicates that the water is not absorbed into the base sheet, which could prevent premature failure of the cooling pad media. Chitosan shows comparable CTQ performance compared to the resin-coated sheet. The results indicate the potential of using chitosan as a paper coating for the HVAC industry in evaporative cooling pads.

Keywords: chitosan, biopolymer, paperboard coating, HVAC, Taber stiffness, wicking

INTRODUCTION

The HVAC industry uses paper to manufacture evaporative cooling pads as a humidifying and air conditioning apparatus for livestock enclosures. Presently, phenol formaldehyde resin is used as a coating component in these cooling pads. This application (paper impregnation) accounts for 8% of the phenol formaldehyde resin used in North America.[1] Phenolic resins are known to increase the dry stiffness of paper and paperboard on a dry basis when used as a coating.[2] However, recent industry reports have indicated premature structural failure of phenolic resin-coated paperboard products when utilized in wet applications, specifically as wet cooling media (pads) for commercial-scale applications. Furthermore, this resin may potentially cause harm to natural aquatic biota if released into the environment at high concentrations.[3] Therefore, there is a need to search for alternative coating materials for paperboard products to be used in wet applications that could not only maintain or improve paperboard wet stiffness and structural integrity, but also be environmentally benign and obtained from renewable sources.

A potential candidate material that can meet these criteria is chitosan. Chitosan is a heterogeneous polysaccharide containing β-(1-4)-linked 2-amino-2-deoxy-D-glucose (glucosamine) units (around 90%) and N-acetyl-2-amino-2-deoxy-D-glucose (N-acetyl glucosamine) units obtained through deacetylation of chitin, which contains a high level of the N-acetyl glucosamine units.[4] Chitosan is the deacetylated derivative of chitin, and is most commonly associated and derived from crustacean shells. However, chitosan obtained from these conventional sources is typically expensive due to the harsh and labor-intensive processes required for the isolation of chitosan from the complex and recalcitrant matrix of the crustacean exoskeleton.[5] The high cost of chitosan has severely limited the potential application of chitosan to high cost specialty products (*e.g.* biomedical and advanced materials) that require high purity starting materials. Fortunately, chitosan can also be produced using microbial cultivation and fermentation processes since chitosan is a major cell wall component of fungal strains

belonging to the order Mucorales and class Zygomycetes.[6] Fungal chitosan is more advantageous than the conventional crustacean-derived chitosan due to the fact that the former can be produced in controlled bioprocesses irrespective of geographical and seasonal situations, in contrast with the latter.[7] Furthermore, fungal chitosan properties can be manipulated to suit the intended applications through the control of bioprocessing conditions.[8] Low cost agro-industrial waste residues may also be utilized as growth substrates for the chitosan-producing fungi to further reduce the cost of the chitosan product.[9] This could permit further expansion of chitosan applications to other fields requiring low-cost bio-based alternatives, such as functional paperboard coating materials.

Previous studies have demonstrated the potential use of chitosan as a functional coating material on paper to improve various mechanical and barrier properties of the paper or paperboard to which it is applied.[10-12] For instance, chitosan has been found to improve mechanical properties, such as stiffness and water resistance.[10] It has also been suggested that the use of chitosan can increase wet strength properties of paper.[12] Chitosan as a coating additive also displays some amount of anti-microbial properties.[13] The potential for microbial growth in the livestock enclosure HVAC application is significant. If chitosan were to be used, it could possibly prevent the growth of microbial bacteria and positively benefit the agriculture sector. Being a bio-based polymer, chitosan also has the favorable characteristic of being biodegradable.[10-11] However, research on the use of chitosan as an alternative to phenolic resins as paperboard coating materials for the evaporative cooling application has been limited. This is the main focus of the current study. Evaporative cooling requires the sheet to maintain stiffness for long periods of time under water-saturated conditions. To produce a better cooling effect, the paper also needs to be able to wick water over the entire paper surface to increase water evaporation as hot air is passed across the surface. In this study, chitosan was used as a functional coating to achieve specific mechanical properties. Commercially available crustacean-derived chitosan was used in the preliminary coating condition studies that required meeting coating application performance benchmarks. Chitosan obtained from fungal grown in the laboratory using agricultural residues was also tested. The specific objective of this study has been to determine the effect of a chitosan coating on paperboard sheet properties with intended application in evaporative cooling of commercial-scale agricultural facilities. These properties include wet stiffness and visually observable wicking height and moisture absorption. The goal of this research is to demonstrate the improvement of the wet stiffness and structural integrity of paperboard, while achieving target performance parameter levels (*i.e.* wicking and water absorption). Taber stiffness is measured as the bending resistance of a sample to bend fifteen degrees at a distance of 50 mm from the clamping apparatus. Chitosan is shown to increase Taber stiffness on a dry basis.[12] However, it was suggested that the use of chitosan could increase wet strength properties.[14] This study was conducted to assess the feasibility of replacing phenolic resins with chitosan as a paper coating for the HVAC industry.

EXPERIMENTAL

Coating preparation

The paper coating solutions were produced in 250 mL batches using commercially available low molecular weight chitosan (CAS: 9012-76-4) purchased from Sigma-Aldrich Inc. (St. Louis, MO). Five grams of chitosan was dissolved in 250 mL of 1% acetic acid dilution to create a 2% w/v solution having a viscosity of 170 cP at 40 rpm with a #4 spindle on the Brookfield rotational viscometer. The mixture was stirred for one hour at the maximum speed (1000-1200 rpm) allowed by the mixture. The coating was then stored at 5 °C until use. Before coating the sheets, the coating was stirred at 600-700 rpm for one hour to ensure homogeneity. For the fungal chitosan formulations, the same procedure was followed as for the commercial chitosan, but the viscosity was too low to measure with the Brookfield instrument, so it can be considered water-like. The fungal chitosan was extracted from *Amylomyces rouxii* ATCC 24905 grown on a soybean meal substrate as described previously.[15]

Coating of paper base sheets

Samples of uncoated and phenolic resin-coated paper (21.5 x 28 cm) were provided by Semper Exeter, Inc. (Covington, KY). Prior to the coating tests, the sample sheets were stored in TAPPI standard conditions as stated at TAPPI standard T-402, 23 °C, 50% RH for at least 72 hours.[16] Two sample sheets were coated to measure coat weight for each condition, so that four samples could be cut and weighed for coating weight estimation.

Uncoated sheets were placed in the sample holder on the Gardner glass topped bench coater platform (Paul N. Gardner Company Inc., Pompano Beach, FL), so that the sample was coated in the machine direction of manufacture. The rod was placed at the top of the sheet and the coating was applied to the sheet near the rod. The rod was then pulled down the sheet at a constant rate. A Noble and Wood steam driven drying can (Noble &

Wood Machine Co., Hoosick Falls, NY), operated at 10 psig of steam, and approximately 220-225 °F internal drum temperature, was used as drying equipment. The coated sheet was sandwiched between two screens and run through the dryer, coating side against the drum for approximately 40 seconds of contact, which is adequate to dry the coating. Samples were then kept at TAPPI standard T-402 (23 °C, 50% relative humidity) conditions for 72 hours prior to testing.[16] Coat weight determinations were made using the Messmer press (Messmer Büchel West Mill Gravesend Kent, United Kingdom), which cuts a sample that is 1/100 of a square meter. Four samples were weighed and the weights were averaged to determine the average approximate coat weight for each experimental test condition, as well as for the phenol formaldehyde resin coated sheets provided. The rod numbers were chosen in order to achieve a similar coat weight for all chitosan-coating conditions. This allowed the results for mechanical property testing to be compared fairly.

Critical-to-Quality (CTQ) parameters testing

Dry and wet Taber stiffness

Dry Taber stiffness was measured according to TAPPI standard T-489.[17] The uncoated, phenol-formaldehyde, and commercial chitosan-coated sheet samples were cut with the sample cutter and tested. Wet Taber stiffness was measured on the Taber V-5 Stiffness tester (Teledyne Taber, North Tonawanda, NY). Wet Taber stiffness was measured using the following customer-specified procedure and conditions. The samples were cut into 2-inch wide by 2.5-inch long rectangles with a challenge guillotine paper cutter (The Challenge Machinery Company, Norton Shores, MI). The industry partner in this project used this size for the test. It is not the TAPPI standard size for this test and should be noted here. Multiple sheets were prepared by this method in both the machine and cross-direction (MD and CD, respectively) of the paper sheet samples to determine if there is a machine cross-directional effect on coating performance. A sample was placed into a bath of tap water that had been equilibrated to room temperature 73 °F, or 23 °C. After 60 seconds, the sample was withdrawn from the water and placed between dry blotter sheets. A 10-kg roller was rolled in both directions over the sample, which was sandwiched between blotter sheets. At least two sheets of blotter were placed on the top and bottom of the sample to ensure good water removal. The sample was then transferred to the Taber stiffness tester and the test was run. The measured wet stiffness values of the samples were averaged together in each direction, MD and CD, respectively. Twenty samples readings were taken from five sample sheets.

Vertical wicking height and mass gain due to water absorption

The vertical wicking test samples were cut with an HA Saydon (England) sample cutter to one inch wide. Three samples were cut from each sheet in the machine direction of manufacture. The sample was weighed on a Sartorius CP225D (Merck Research Laboratories) scale and the weight was recorded to four decimal places. The sample was then attached to the sample holder so that the sample was held perpendicular to the water interface. A jack stand and a Pyrex dish, filled with de-ionized water that had been allowed to equilibrate to room temperature, were positioned under the sample holder. The jack stand was elevated until the sample just broke the surface of the water. A timer was started when the surface of the water was broken by the sample. When ten minutes had passed, the jack stand was lowered and the sample was removed and measured to the nearest 1/16 of an inch. The cut sample was then weighed after the measurement was taken and recorded to four decimal places. The weight of water absorbed, percent weight gained and the absorption weight per unit area (g/m^2) absorption were calculated in Excel. This test was also conducted on uncoated, phenol formaldehyde-coated, and chitosan-coated sheets.

RESULTS AND DISCUSSION

Coating conditions to achieve desired coat weight

The coatings were initially applied with #30 and #42 Meyer rods coated on one side to achieve the desired 3.5 g/m^2 coat weight. This weight was chosen based on previous research by Kuusipalo and colleagues.[12] A #20 rod was used to coat one layer on both sides of the sample with commercial chitosan, and a #11 rod was used to coat one layer on both sides with fungal chitosan. These conditions achieved a coat weight near the desired coat weight of 3.5 g/m^2, compared to 22.4 g/m^2 for the phenol formaldehyde resin coated sheets. Multiple sheets were then coated for each of these combinations for CTQ parameter testing.

Effect of chitosan on Taber stiffness

Taber stiffness is measured as the resistance of a sample to bending fifteen degrees at a distance of 50 mm from the clamping apparatus.[17] The effect of different coating conditions on the bending resistance (Taber stiffness graph) is shown in Figure 1.

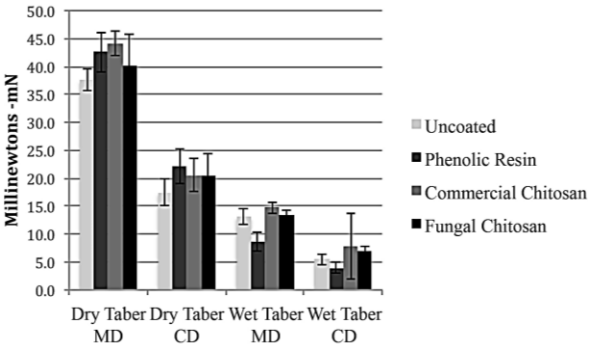

Figure 1: Taber stiffness for different conditions

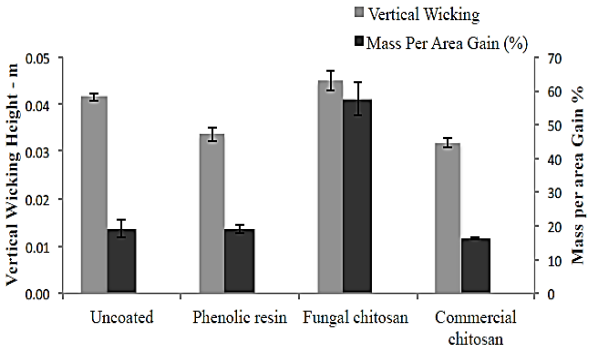

Figure 2: Vertical wicking and mass gain

The fungal and commercial chitosan-coated samples had higher wet Taber stiffness than phenolic resin, under wet conditions. The fungal chitosan coated sample had a MD wet stiffness of 13.34 mN, while the commercial chitosan had a wet Taber stiffness of 14.71 mN. These are significantly higher than the wet stiffness value of the phenolic resin, which was 8.83 mN. It is believed to occur because while chitosan is hydrophilic, it allows the sheet to retain greater stiffness than the phenolic resin due to the lower coat weight. A previous study by Kuusipalo *et al*.[12] has shown that chitosan significantly increased Taber stiffness on a dry basis.

Effect of chitosan coating on water wicking and absorption

Vertical wicking is an important parameter of evaporative cooling. According to Kuusipalo *et al*.,[12] the water absorption of paper coated with chitosan decreases with increasing coating weight, which was attributed to non-uniform film formation. Research indicates that chitosan coatings display high surface hydrophilicity.[11,13] This hydrophilicity should allow for a balance to be achieved between wet stiffness and vertical wicking. It is important to note that while chitosan does not create a barrier to water, it does improve the water holdout of the paper, because the chitosan fills the voids in the porous structure of the paper.[11-12] The chitosan-coated, phenol formaldehyde-coated, and uncoated samples were run at the customer specific conditions of 73 °F or 23 °C, and 50% relative humidity. The results for the vertical wicking and mass gain due to water absorption are shown in Figure 2.

In terms of vertical wicking, the data show that fungal chitosan outperforms the phenolic resin. The mass gain and area per mass gain is also important to the HVAC application. If a higher mass of water is present, the evaporative cooling media has the potential for inefficiency. If the same mass of water is present, but has increased surface area, the evaporative cooling media can be much more effective. Figure 2 illustrates how chitosan compares with phenolic resin. The data seem to indicate that even though the wicking height is higher, more water is being drawn further into the sheet in the fungal chitosan coated sample. The extra weight may contribute to the premature failure of these evaporative cooling media. The commercial chitosan product seems to perform better than the fungal chitosan in this test parameter. The increased wet strength conferred by the fungal chitosan coating may alleviate this potentially negative effect and function properly in the cooling wick.

CONCLUSION

The use of chitosan as a paperboard coating shows promise for investigation based on this research. The papers coated with chitosan display equally as good, or better, water wicking properties as paper coated with phenol formaldehyde resin. Commercial crustacean shell chitosan-coated paper sheets were also found to absorb less moisture weight than the phenolic resin-coated paper sheet. This indicates that water absorption is only taking place on or near the surface of the commercial chitosan-coated sheet. The water absorption of the resin-coated and fungal chitosan-coated sheet seems to show a penetration of the water into the base sheet of the evaporative cooling wick. The preliminary wet strength data seem to indicate that the sheet coated with chitosan maintains wet strength better than the phenolic resin-coated sheet. Chitosan shows good potential for use in other applications that require similar properties from paper and paperboard. Future work should evaluate whether increasing the coating weight has a positive impact on CTQ properties. Chitosan can be made from by-products of multiple industries. It is a bio-based product that is sustainable and renewable, and has the positive

characteristic of being biodegradable.[11,13] Additionally, chitosan as a coating additive displays some amount of antimicrobial properties.[13] These characteristics and the research completed in this study support the continued evaluation of chitosan in industrial applications and particularly its potential use in livestock enclosure HVAC applications.

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