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Biodegradable chitosan coating for wood protection

A Andok and M S G Jesuet*

Faculty of Tropical Forestry, Universiti Malaysia Sabah, Jalan UMS, 88400, Kota Kinabalu, Sabah, Malaysia

*Corresponding author: melissa.gilbert@ums.edu.my

Abstract. Chitosan coating is a biopolymer-based coat made out of modified chitin that is usually derived from shellfish. The general development of the chitosan coating was to provide adequate, albeit impermanent, lamination of food products for protection during long transportation. With the idea for a *pro tempore* coating, this study focused on the production of a transient coating made from cockle shells-derived chitin, for the temporary protection coating for pre-machined wood instead. Due to its solubility in organic acids, the purpose of the coating primarily focused on the protection of pre-machined wood that is high in moisture content and susceptible to damages, in which will allow the easy removal of said coating whenever necessary. The process started with the extraction of chitin from the cockle shells through the demineralization, deproteinization, and deacetylation steps before integrating it with starch and glycerol to produce the biodegradable coating. The aim of this study was to determine the effect of the different deacetylation time (30, 60, and 90 minutes) on the physical and chemical properties of the coating. The physical properties observed includes the water absorption, drying time, various temperature resistance, and viscosity, meanwhile the chemical properties were observed based on its infrared spectra identification and pH value. Based on the results, the samples with the longest deacetylation time of 90 minutes displayed the best physical properties with a lower water absorption, shorter drying time, lower pH value, and best resistance towards the various temperature cycles, as compared to the other samples. This evidently shows the importance of the deacetylation process, as well as a sufficient hydrolysis prolongation in producing a desirable chitosan coating quality.

Keywords: Chitosan; coating; deacetylation.

1. Introduction

Wood deteriorates rapidly even in moderate environmental through a variety of biotic processes [1]. The major applications for wood coatings and preservatives are mainly used for wooden furniture, decking and siding manufacturing. The coating of wooden surfaces serves mainly for surface protection and thus increases their utilization by not limiting the use of wood for interior purposes only. The development of wood coating nowadays is progressively inclined towards a more environmentally friendly biopolymer materials.

Over the past several decades, several biopolymers have received increased attention for their application such as in chemicals, biomedical, and food industries, in which one of them is chitin. Chitin is an abundant naturally occurring biopolymer and can be found in the exoskeleton of crustaceans, in fungal cells walls and in other biological materials [2]. Conversion of chitosan chemically from chitin involves demineralization, deproteinization, and deacetylation [3]. The extraction of chitin had high reproducibility in shorter time, simpler manipulation, smaller solvent consumption and lower energy input. Chitosan derived from chitin has high antimicrobial activity against various microorganism, thus are known to produce antimicrobial edible films and coatings [4].

In this study, a semi-permanent chitosan biopolymer wood coating was produced from modified chitin from cockle shells, glycerol, and starch. Different deacetylation durations play the important part in the quality of chitosan, hence three (3) different deacetylation time of 30, 60, and 90 minutes were



observed. The effectiveness and suitability of the chitosan wood coating was evaluated based on its physical and chemical properties within the three (3) different chitosan produced from the three (3) different deacetylation duration mentioned before.

2. Experimental

2.1 Material preparation

The cockle shells were locally obtained as the source of chitin. Alternatively, *Acacia mangium* wood panel (30×15cm) was used for application with chitosan coating. Chemicals such as hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Sigma Aldrich.

2.2 Chitin conversion

2.2.1 Demineralization. One of the commonly isolated chitin from cockle shells is by demineralization (calcium carbonate and calcium phosphate separation) [5]. Demineralization was carried out by adding 5L of 4% of HCl to 550g of grounded cockle shells. Solution was constantly stirred at room temperature under a 250-rpm turbulence for the predetermined duration. The demineralized shells were then filtrated and washed with distilled water, then dried in an oven at 70°C for 24 hours.

2.2.2 Deproteinization. Deproteinization involves the removal of proteins by using 4% of NaOH to the dried demineralized shells powder in a beaker with solid/liquid ration of 50:500 (g/ml). The reaction was carried out under agitation at 30°C room temperature for 19 hours. The solid was filtrated and washed with distilled water until it achieved neutral pH and the resulting chitin was dried in an oven at 70°C overnight [5].

2.2.3 Deacetylation. Deacetylation of chitin is a process to produce chitosan through the hydrolysis of the acetamide groups. Deacetylation of chitin was conducted by reacting the chitin with 40% NaOH at a solid/liquid ratio of 500:7.5 (g/L) in beaker. The deacetylation process with NaOH were distinguished following three predetermined durations of 30, 60, and 90 minutes, which are henceforth referred as D30, D60, and D90 sample respectively. The resulting chitosan was filtrated and then washed with distilled water until neutral pH was obtained and then followed by an overnight oven drying at 70°C [5].

2.3 Coating preparation

Chitosan coating were produced through the combination of chitosan, glycerol, and tapioca starch [6]. The chitosan solution was prepared by adding the glycerol into the dry weight of starch to produce a starch-glycerol solution of 25% w/w of the dry starch solid weight. All dispersions were heated in 80°C water baths with continuous stirring until gelatinized completely and followed by cooling process to room temperature. 20g chitosan flakes were dispersed in 100ml acetic acid 1% v/v in a beaker and stirred in order to dissolve the biopolymer. The dispersion was heated in 80°C for 60 min under continuous stirring to completely liquefy the chitosan [7]. The coating solution was prepared by mixing the liquefied chitosan with the starch solution in 1:1 ratio and stirred further for 20 minutes.

2.4 Physical characterization of chitosan coating properties

2.4.1 Water absorption. This test method is to determine the effective water repellence of the coating by immersing a fully coated wood in water for 24 hours. This process allows the observation of weight increase from before and after the plunge. The increase of weight could be evidence of the penetrability of water through the coating, indicating a poor coating trait.

The weight difference determination follows equation (1):

$$\text{Water Absorption, (WA)} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where:

WA= Water absorption (%)

W_0 = Initial weight of coated wooden sample before immersion in water (g)

W_1 = Final weight of coated wooden sample after immersion in water (g)

2.4.2 Drying time. Drying of coating was performed in room temperature to identify the duration of the coating to be fully dried through the dust-free method. The determination of the drying of the coating was tested every 10 seconds, in which a surface of the wooden block was sprinkled with sawdust. The indication of a dried coating is a dust-free surface, or whenever the sawdust does not adhere to the surface anymore. The drying time is determined by Standard Test Methods for Drying, Curing or Film Formation of Organic Coatings from ASTM D1640 based on various stages and rates film formation in the drying of organic coating under condition of ambient room temperatures [8].

2.4.3 Endurance of various temperature cycles. Durability of coating against various temperature change was determined through the various temperature cycles test, where the coated wooden block must endure a number of changes that mimics a day to day or season to season changes in temperature. One cycle of test includes a one (1) hour session in cold condition (-10°C), followed by an hour in room temperature for conditioning, and then followed by another one (1) hour in hot condition (50°C). The wooden blocks are then conditioned for another hour in room temperature to allow the observation of coating defects. The cycle was then repeated again until defects emerges, or a maximum of ten (10) cycles.

2.5 Chemical characterization of chitosan coating solution properties

2.5.1 Viscosity. Viscosity is defined as resistance to flow and is affected by the presence of intermolecular force in a liquid solution. Higher intermolecular force is the result of a high attractive force between the molecules of the same type, hence increasing the cohesiveness and viscosity. Higher viscosity means more resistance to flow of fluids such as gases and liquids [9]. The different samples of coating solution was tested using the Brookfield CAP 2000 Viscometer multispeed digital cone-plate to obtain its viscosity. The viscosity affects the spreading rate during coating but also crucially substantiate the presence of chitosan which characteristically dissolves greatly in water.

2.5.2 Infrared spectra via Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectroscopy was used to identify the resulting interaction between chitosan and glycerol-starch solution. The absorbance of the blending materials was determined by the IR spectrum and concentration of liquid sample. The infrared spectra were observed by scanning at a cm^{-1} resolution for transmission wavelength range of 40000 to 4000 cm^{-1} .

3. Results and discussion

3.1 Physical properties: Water absorption

Based on the results in Figure 1, there is a difference in the water absorption abilities of the three different deacetylation time samples. The result shows that the absorption rate was 51%, followed by 48.8%, and 47.7% for the D30, D60, and D90 samples respectively, which indicates that the D30 samples uptakes the highest amount of water. As the D30 materials underwent the shortest time for deacetylation, the removal of the acetyl group were incomplete, hence producing a product with a lower degree of deacetylation or containing higher non-deacetylated chitin. The incomplete chitin-chitosan hybrid was shown to be less stable and are more easily penetrated by water, hence allowing the higher moisture transport. According to [10], the accumulation of water or moisture provides an optimal decay condition in wood, in which a high water absorption rate on a fully coated wood affirms the inferior quality of the coating itself.

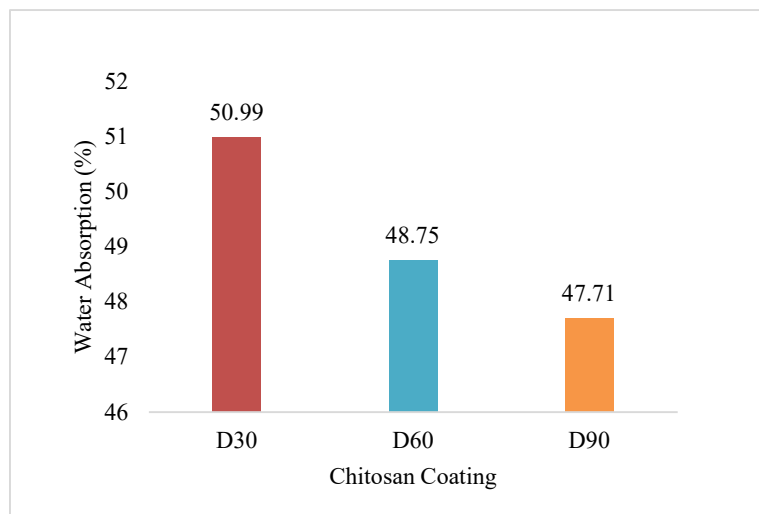


Figure 1. Water absorption of different deacetylation duration samples.

3.2 Physical properties: Drying time

Based on the results in Figure 2, there is a noticeable downward shift in drying time from the D30 towards the D90. It shows that the shorter the deacetylation time, the longer the drying time will be, as shown from the deacetylation for D30 samples that takes 175 seconds compared to the 85 seconds for both D60 and D90 samples. This shows that the different acetylation time does affect the properties of the coating samples, as the acetyl group was not entirely eliminated in the shortest deacetylation duration process which resulted in a hybrid chitosan-chitin of a lower degree of deacetylation product. According to [11], the acetyl groups are removed through the deacetylation process of chitin, thus resulting to the lower hydrogen bonded, hydrophobic chitosan. The longer drying time of the D30 samples attested the insufficient time for the deacetylation time through the presence of the hydrophilic chitin content, in which was additionally supported by the water absorption rate in Figure 1.

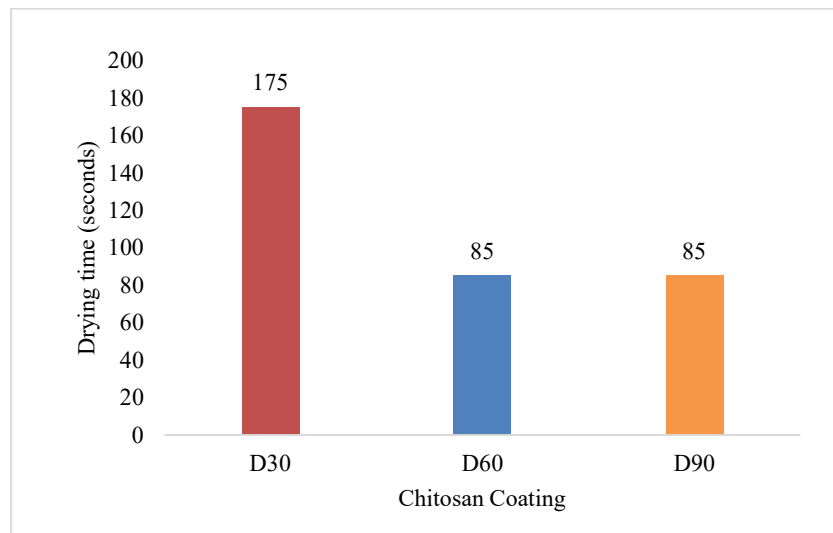


Figure 2. Drying time of different deacetylation duration samples.

3.3 Physical properties: Endurance of various temperature cycles.

Based on the various temperature cycle test, at a maximum of ten (10) cycles, no coating deterioration was observed. Therefore, the observation shifted on the change in colour instead. From Figure 3, it is shown that colour changes happened on all three coating samples with different degree, with the samples of D30 and D60 showing higher changes, however not substantially notable. The deacetylation duration may affect the colour changes due to the availability of the residual chitin, unable to be converted to

chitosan due to the short period of deacetylation. Based on the findings by [12], chitosan and chitin has comparable colours from each other, with chitosan appearing slightly fairer than chitin. Through heat treatment that is similarly mimicked by the hot condition (50°C) in the endurance test, it was reported that colour changes may happen due to the chemical binding of pigments resulting from the high temperature.

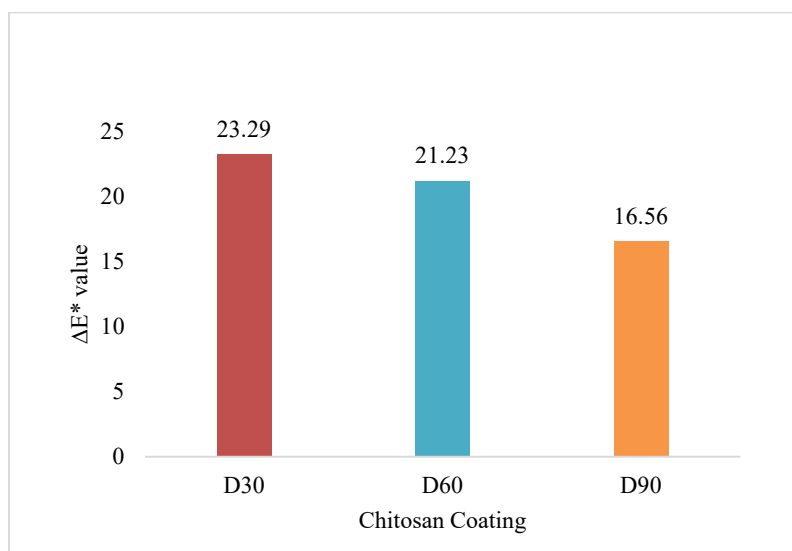


Figure 3. Samples colour change after various temperature cycles.

3.4 Chemical properties: Viscosity

Based on Figure 4, the coating samples of different deacetylation time shows significantly (0.00) different viscosity value against the 30 minutes samples. It shows that the viscosity value decreased as the deacetylation duration increased, with 3.5, 2.2, and 1.7 cP viscosity for the D30, D60, and D90 coating samples respectively. According to Lewandowska *et al.* (2015), viscosity of a solution or blend relies heavily on the intermolecular interactions of the composition, which includes hydrogen bonding amongst other [13]. Higher attractive force between molecules of the same type produces a higher viscosity as in the D30 sample, indicating a higher hydrogen-bonded chitin, making the solution highly viscous.

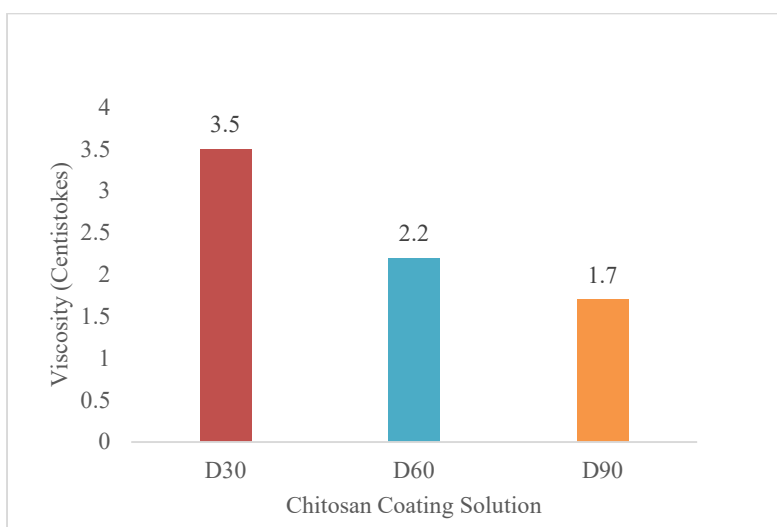


Figure 4. Viscosities of different deacetylation duration solution samples.

3.5 Chemical properties: Infrared spectra

The comparison spectrum graphs of different deacetylation obtained are shown in Figure 5. From the infrared spectra shown, there were attributed to axial OH and NH group vibrations ($3600 - 3200 \text{ cm}^{-1}$), which are more evident in the chitosan spectra. In each sample of chitosan, there are three or more significant points of frequency such as carboxylic acid ($3300 - 2500 \text{ cm}^{-1}$), alkene ($1648 - 1638 \text{ cm}^{-1}$) and alcohol ($1420 - 1330 \text{ cm}^{-1}$). However, the D90 coating samples has an additional nitro compound ($1550 - 1300 \text{ cm}^{-1}$) and hydroxyl group ($1320 - 1210 \text{ cm}^{-1}$) that shows the ongoing process of the severing of the acetamide bond, which may be the effect of the longer deacetylation that involves the elimination of acetyl group or acetamide to produce linear polysaccharide chitosan. The presence of the alkyne group which consist of the tottery $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ evidently shows the incomplete chemical conversion, due to the necessary stabilizing effect of the double and triple bonded carbons, thus showing signs of instability of the D30 and D60 samples.

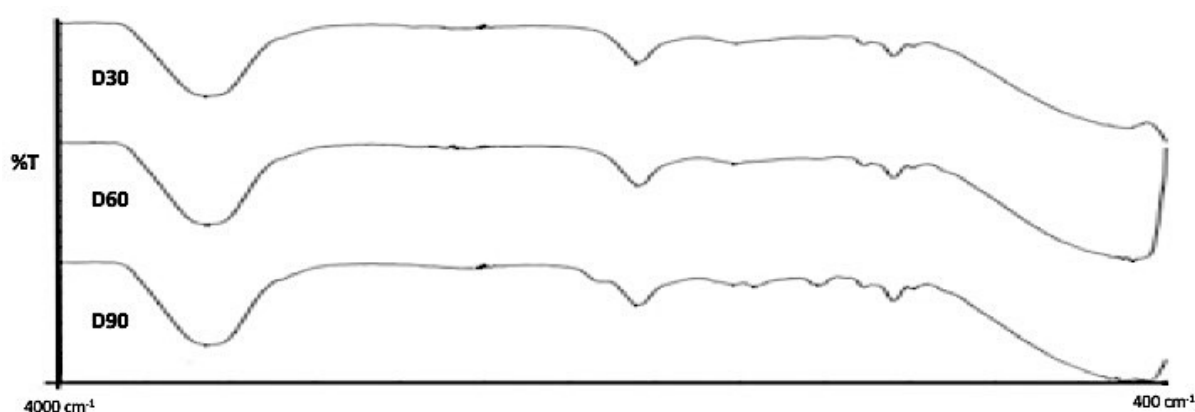


Figure 5. Infrared spectra of different deacetylation duration chitosan coating solution samples.

4. Conclusion

The physical and chemical properties of semi-permanent chitosan coating was obtained. Based on the different deacetylation duration on all three samples, which includes the 30, 60, and 90 minutes proves to be affecting the properties of the coating. The D90 sample, which has the longest deacetylation duration of 90 minutes shows a more superior hydrophobic characteristic, which is an advantage for a coating, with the lowest water absorption and shortest drying time. However, the deterioration based on the various temperature cycles test showed that the three samples does not show any visible defects on the coating apart from the colour change, with D90 exhibiting the lowest colour shift. As for the chemical properties, the viscosity showed a higher internal friction in the D30 and D60 samples, compared to the D90 samples, which indirectly showed the higher chitosan content in D90 samples due to its higher water solubility. As for the identification of functional group from the infrared spectra, the D90 samples showed a better and more stable structure by the absence of the alkyne group which consist of the precarious $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$, which is present in the D30 and D60 samples.

5. References

- [1] Blanchette R A, Haight J E, Koestler R J, Hatchfield P B and Arnold D 1994 Assesment of deterioration in archaeological wood from ancient Egypt. *J Arn Inst Conserv* **33** 55-70
- [2] Elsabee M Z and Abdou E S 2013 Chitosan based edible films and coatings: A review. *Materials Science and Engineering: C* **33**(4) 1819-1841
- [3] Shanta P, Ralf L, Wolfgang G, Andre W, Werner L, Reinhold G, Paras N Y and Rameshwar A 2016 Synthesis of chitosan from prawn shells and characterization of its structural and antimicrobial properties. *Nepal Academy of Science and Technology* **17**(1) 5-9
- [4] Dutta P K, Ravikumar M N V and Dutta J 2009 Chitin and chitosan for versatile applications. *JMS Polym Rev* **42** 307

- [5] Younes I and Rinaudo M 2015 Chitin and chitosan preparation from marine sources: Structure, properties and applications. *Mar. Drugs*. **13** 1133-1174
- [6] El-hefian A E and Yahaya A H 2010 Effects of temperature, shearing time and rate of shear on the viscosity of chitosan/agar-blend solutions. *Maejo International Journal of Science and Technology* **4**(02) 261-267
- [7] Chillo S, Mastromatteo M, Conte A, Gerschenson L and Del Nobile M A 2008 Influence of glycerol and chitosan on tapioca starch-based edible film properties. *Journal of Food Engineering* **88**(2) 159-168
- [8] ASTM D 1640 Standard Test Methods for Drying, Curing or Film Formation of Organic Coatings. *ASTM International, West Conshohocken PA* 2018
- [9] Renata C R, Ivano A D, Gabriel H H O, Paulo C C, Diego P R A, Athina B M S and Claudia O S 2014 Mechanical properties permeability and solubility of films composed of yam starch and glycerol. *Interciencia* **39**(6) 410-415
- [10] Van Meel P A, Erich S J F, Huinink H P, Kopinga K de Jong J and Adan O C G 2011 Moisture transport in coated wood. *Progress in Organic Coatings* **75** 686-694
- [11] Roy J C, Salaün F, Giraud S and Ferr A 2017 Solubility of chitin: Solvents, solution behaviors and their related mechanisms. *Solubility of Polysaccharides* Intech Open
- [12] Tamzi N N, Faisal M, Sultana T and Ghosh S K 2020 Extraction and properties evaluation of chitin and chitosan prepared from different crustacean waste. *Bangladesh Journal of Veterinary and Animal Sciences* **8**(2) 69-76
- [13] Lewandowska K, Sionkowska A and Grabska S 2015 Influence of the Intermolecular interaction on physico-chemical properties of chitosan/hyaluronic acid blends. *Progress in the Chemistry and Application Chitin and its Derivatives* **20** 170-176