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Contributed Paper

Preparation of Depolymerized Chitosan and Its Effect on Dyeability of Mangosteen Dye

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ABSTRACT

The preparation of chitosan having various low molecular weights was carried out by treatment with sodium nitrite in acid media. The intrinsic viscosities of resultant chitosans designated to CTS-MW I, CTS-MW II, and CTS-MW III were measured for the determination of chitosan's molecular weights using Mark-Houwink-Sakurada equation. As a result, the molecular weights of CTS-MW I, CTS-MW II, and CTS-MW III were 226 kDa, 10.8 kDa, and 7.2 kDa, respectively. In addition, thus obtained chitosans were characterised by infrared spectroscopy in order to determine the degree of deacetylation and nitrogen content. It was found that the molecular weight values as well as nitrogen content decreased with an increase in the amount of sodium nitrite. The opposite held true in case of percent degree of deacetylation. The application of chitosan onto cotton fabrics was also carried out. The effect of chitosan concentrations was studied. The results showed that percent nitrogen content tended to increase with an increase in the concentration of the depolymerized chitosans. Then, the co-application of chitosan and mangosteen dye extract on cotton fabric was carried out using three dyeing methods, namely, all-in-one method, pre-dyeing method, and post-dyeing method. It was found that the pre-dyeing method showed higher colour strength values in all cases. The effects of chitosan concentration and their molecular weights on colour fastness and fabric stiffness were also studied. The finding showed that chitosan with low molecular weights insignificantly imposed stiffness problem due to the lack of chitosan film formation on the fabric surface.

Keywords: depolymerized chitosan, mangosteen dye extract, depolymerization, cotton fabric.

1. INTRODUCTION

Chitosan is a useful biopolymer obtained by alkaline deacetylation of chitin. Generally, chitin is converted into chitosan with various degrees of deacetylation (DD) and molecular weights (Mw) depending upon the purpose of chitosan utilization [1-3]. Chitosan differs from chitin in that it is soluble in mild acidic medium. The cationic form of chitosan in acidic solution plays a role in not only governing its solubility but also acting as an active site. The applications of chitosan for improving dyeability of cotton fabric has been widely studied [4-6]. In the textile area, the higher the active site of chitosan favors the higher the dye adsorption (including natural dye) as well as film formation on fiber surface [7]. Chitosan film on fabric surface is not desirable since it causes the problem of fabric stiffness (poor handling) [4, 8]. Fortunately, these effects could be adjusted by the usage of chitosan's proper molecular weight. Normally, chitosan with various molecular weights could be achieved by depolymerization techniques.

In this study, the depolymerization of native chitosan using sodium nitrite under mild acidic condition was proposed in order to prepare chitosans with various low molecular weights [7]. Then the obtained depolymerized chitosans and mangosteen dye extract as a colorant were applied onto cotton fabrics. To investigate the co-application of chitosan and mangosteen dye extract on cotton fabric, three dyeing methods, namely, all-in-one method, pre-dyeing method, and post-dyeing method were compared. The dyeing properties including dyeability, colour fastnesses, i.e. light fastness, wash fastness, and fabric stiffness were evaluated.

2. MATERIALS AND METHODS

Woven cotton fabric and fresh mangosteen leaves; *Garcina mangostana*, were obtained from Keerewong village located at Nakornsrithamrat province, Thailand. Soap nut scoured cotton fabrics sized 30×30 cm^2 (120 g/m^2) and mangosteen leave aqueous extract were prepared in the laboratory and used throughout. The colorants found in mangosteen extract include xanthone and tannins [9]. The chemical structures are presented in Figure 1.

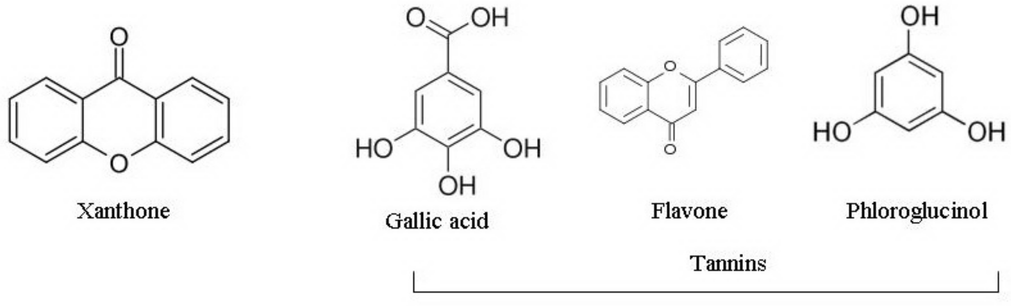


Figure 1. Chemical substances found in *Garcina mangostana.*

The scouring conditions used were 20 g/L soap nut extract (natural surfactant) with pH value of 3.8 and scouring temperature of 90°C for 40 minutes. The scoured fabric with soap nut extract showed adequate absorbency for dyeing with a natural dye. Commercial grade of chitosan powder (approx. 85% DD with Mw of $2x10^2$ kDa) purchased from Ebase Co., LTD (Thailand) was used. Analytical grade chemicals used in this study were bought from Labscan (acetic acid; CH_3COOH, methanol; CH_3OH, and acetone; $(CH_3)_2CO$), Univar (sodium hydroxide; NaOH, and sodium nitrite; $NaNO_2$), and Unilab (hydrochloric acid; HCl).

2.1 Preparation of Chitosans Having Low Molecular Weights

The depolymerization of chitosan using sodium nitrite in acid media was carried out to obtain the chitosan samples with various molecular weights. Three sets of different chitosan solutions were prepared by dissolving 6.0 g of chitosan in each 300-mL of 2% (v/v) acetic acid solution and allowed to stand overnight at room temperature (RT). The prepared solution was designated to "chitosan solution". Various amounts of $NaNO_2$, i.e. 0 g, 0.179 g (3% w/w), and 0.543 g (9% w/w) were added into three chitosan solutions designated as CTS-MW I, CTS-MW II and CTS-MW III, respectively. The solutions were slowly stirred at 500 rpm (Framo^R Geratetechnik M 22/1) for 3.5 hrs at 30°C, and then neutralized with 0.1 M NaOH. The solutions were concentrated by rotary evaporator (Buchi Labortechnik AG : R-124/V) at 50-60°C until about 60 mL concentrated solutions were obtained. To extract the chitosan samples, the concentrated solutions were poured into 100 mL methanol. The precipitates were collected by filtration, washed several times with acetone, then dried overnight at RT. The chitosan samples were kept in refrigerator prior to the determination of the degree of deacetylation and the average molecular weight.

2.2 Determination of Degree of Deacetylation

The depolymerized chitosan samples were characterised by potentiometric titration to determine the DD value [1]. Each chitosan samples (0.5 g) were dissolved in 25 mL of 0.1 M HCl and made up to a volume of 100 mL with distilled water. The solution was then titrated with a titrant of 0.05 M NaOH. The pH meter (SevenEasy S-20; METTLER TOLEDO) was used for pH measurement under continuous stirring. The titrant was added until the pH value reached 2.00, and then 0.05 M NaOH was added stepwise, the pH values of solution were recorded, and a curve with two inflection points of each chitosan sample was plotted. The percent degree of deacetylation was calculated using following equation [2] :

$$DD = [203Q/(1+42Q)] \times 100\% \qquad (1)$$

where $Q = N\Delta V/m$, ΔV is the volume of NaOH solution between two inflection points (in L), N is the concentration of NaOH (0.05 M), and m is the dry weight of chitosan samples (g) [1].

2.3 Infrared Spectroscopy

Infrared (IR) spectra of chitosans were recorded on a Shimadzu 8900 FTIR. A sample was prepared in KBr pellet disc. The measurement was conducted using transmission mode at frequency ranges of 4,000-400 cm^{-1} with 64 consecutive scans at 4 cm^{-1} resolution.

2.4 XRD Analysis

XRD diffraction was performed using a PW 3710 Philips diffractometer with CuKα radiation operated at 40 kV and 30 mA. The diffraction patterns were obtained from 2° to 30° at scanning rate of 1° min^{-1}.

2.5 Average Molecular Weight Calculation

The average molecular weight (M_v) of chitosan was calculated with the Mark-Houwink-Sakurada equation using intrinsic viscosity ([η]) and the chitosan-acetic acid interaction parameters k and α at 30°C [2]. The parameters of k and α are empirical coefficient dependent on the degree of deacetylation of chitosan [7].

$$[\eta] = k M_v^{\alpha} \text{ (acetic acid)} \qquad (2)$$

where $k = 1.64\times10^{-30}\times(DD\%)^{14}$

and $\alpha = -1.02\times 10^{-2}\times (DD\%)+1.82$

2.6 Nitrogen Content in the Chitosan

The nitrogen (N) content of chitosan obtained from depolymerization process was measured by Kjeldhal method [6]. The nitrogen content was calculated using the following equation:

$$N = \frac{(V_{sp} - V_{blk})\times [HCl] \times 14.007}{W \times 1000} \times 100\% \qquad (3)$$

where $[HCl]$ is the concentration of hydrochloric acid (0.1 M), V_{sp} and V_{blk} are the volumes of hydrochloric acid (in mL) used for the titration of chitosan samples and blank, respectively, and W is the weight of chitosan (1.0 g).

2.7 Application of Chitosans onto Scoured Cotton Fabrics

The pad-batch application of chitosan was carried out. The soap nut scoured cotton fabrics were padded in chitosan solutions at various concentrations. Typical procedure was conducted as follows: three chitosan solutions having concentrations of 2, 6, and 9 g/L (CTS-MW I) along with four chitosan solutions of 9, 19, 28, and 38 g/L (in case of CTS-MW II and CTS-MW III) were prepared. Then, cotton fabrics were impregnated into the prepared solutions using a laboratory padding machine (Labtec Co) set a pressure nip to achieve 90% wet pick-up. The padded fabric samples were kept in sealed plastic bags at RT for 3 hrs, rinse with warm water, then dried using a laboratory mini dryer (Rapid Labortex Co. Ltd, Taipei, Taiwan) at 70°C for 10 min. Chitosan fabrics were achieved and employed later for co-application of chitosan and mangosteen extract dye on cotton fabric (pre-dyeing method).

2.8 Co-Application of Chitosan and Mangosteen Extract Dye on Cotton Fabric

Three dyeing methods, i.e. all-in-one method, pre-dyeing method, and post-dyeing method, were employed with respect to the chitosan application. To control the materials used for individual methods, two different molecular weights with desired concentrations of chitosan, i.e., CTS-MW I (9 g/L), and CTS-MW II (38 g/L) were carried out.

The all-in-one method was conducted by immersing the scoured fabrics into 60 mL of mixture solution containing chitosan and mangosteen aqueous extract using the liquor to material ratio (L:R) of 5:1 at 60°C for 3 hrs.

The pre-dyeing method was carried out as follows: the scoured fabrics were impregnated into 10 mL chitosan solution using a padder. The padded fabrics were kept in sealed plastic bags at RT for 3 hrs, then dyed with 100 mL mangosteen aqueous extract at 60°C for 1 hr using the method similar to the all-in-one process.

For the post-dyeing method, the scoured fabrics were firstly dyed in 100 mL mangosteen aqueous extract at 60°C for 1 hr. The dyed fabrics were padded with 10 mL chitosan solution and batched at RT for 3 hrs. It was noted that all cases of dyed fabrics were rinsed by tab water to remove surface dye.

2.9 Properties Evaluation

Colour values of dyed fabrics were evaluated using reflectance spectrophotometer (Machbeth colour-EYE 7000). The colour value or colour strength was expressed as *K/S* value. The colour fastness of dyed fabrics was assessed according to the standard methods including ISO 105-B02: 1994(E) for light fastness, and ISO 105-C10: 2006(E) Test no. A (1) for 30 min. at 40°C for wash fastness.

The stiffness values of chitosan treated and untreated dyed fabrics were assessed according to the standard method; JIS L 1096: 1999 Method A (45° Cantilever Method). The samples were tested for warp and weft directions.

3. RESULTS AND DISCUSSION

3.1 Characterizations of Depolymerized Chitosans

IR spectra of chitosan samples are presented in Figure 2. From Figure 2, the distinctive band of carbonyl group found at 1,680 cm^{-1} is clearly observed, indicating that some of the acetyl group still remains in chitosan backbone. After being treated with sodium nitrite, the decrease in the intensity of carbonyl band is observed, implying the

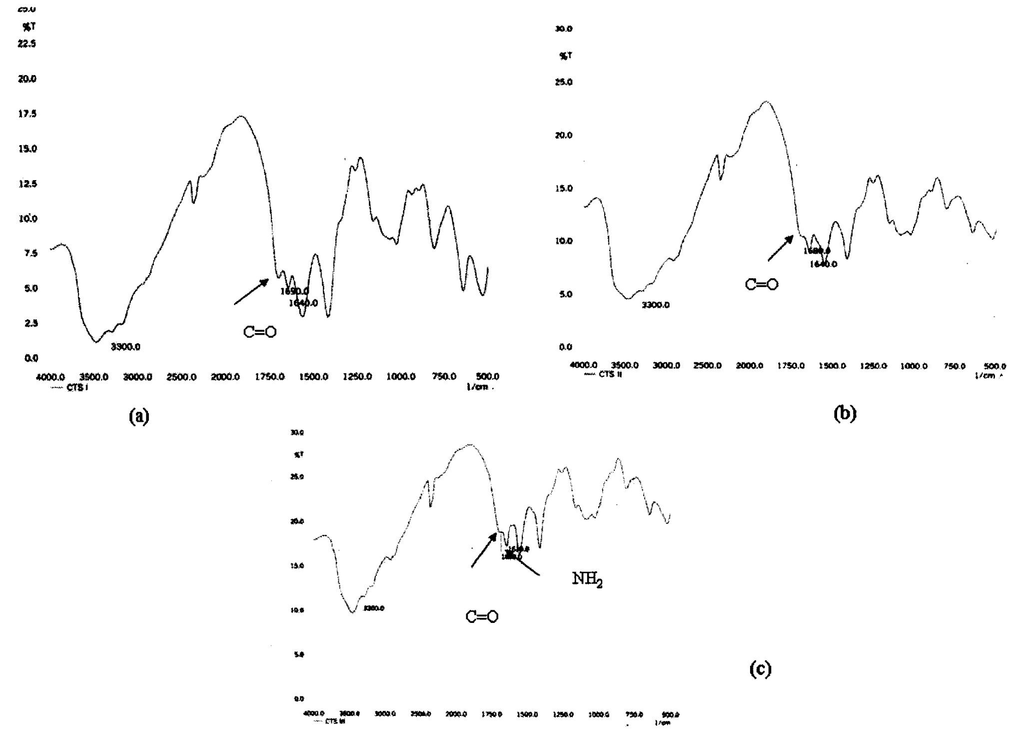


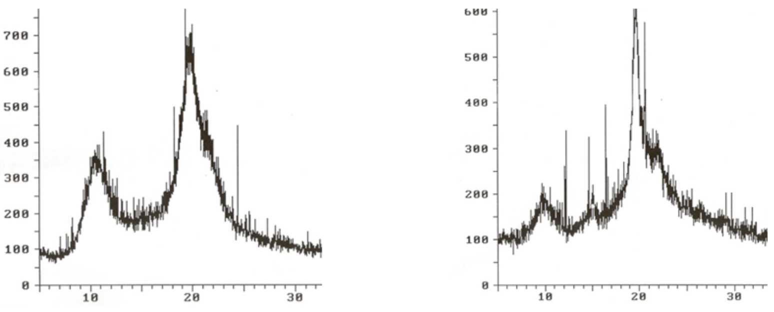
Figure 2. FTIR spectra of (a) native chitosan (CTS-MW I), and depolymerized chitosans i.e., (b) CTS-MW II, and CTS-MW III.

further deacetylation of remaining N-acetyl groups arising from sodium nitrite treatment. In addition, quantitative measurement was determined by potentiometric titration. Table 1 shows percent DD, percent N and M_v of native chitosan (CTS-MW I) and depolymerized chitosans (CTS-MW II, and CTS-MW III).

Table 1. Effect of sodium nitrite concentration on percent DD, M_v, and percent N of chitosans.

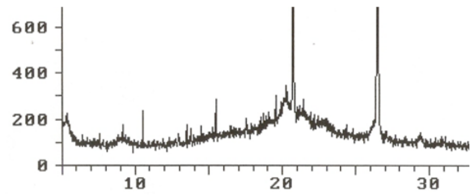
Chitosan Samples	$NaNO_2$ (%w/w)	DD%	M_v (kDa)	N(%)
CTS-MW I	0	96.64	226	7.3
CTS-MW II	3	97.93	10.8	6.4
CTS-MW III	9	99.91	7.2	5.9

The XRD diffractograms of chitosan samples including native chitosan and depolymerized chitosans are shown in Figure 3. The broad peak found at the 2θ = 15° to 30° represents the semicrystalline characteristic of a typical chitosan. From Figure 3 (b) and (c), CTS-MW II and CTS-MW III exhibit a similar XRD pattern to those of native chitosan, but as the amount of sodium nitrite increases so the intensity of the 2θ = 15° to 30° peak is reduced. This phenomenon can be attributed to the fact that the polymer chain of depolymerized chitosan tends to be loosely packed when compared to high Mw chitosan like a native one. As a result, the degree of crystallinity of depolymerized chitosan decreases and directly depends on the amount of sodium nitrite; the more the amount of sodium nitrite the lower the Mw of chitosan with low crystallinity.



(a) Native CTS

(b) CTS-MW II



(c) CTS-MW III

Figure 3. XRD diffractrograms of (a) native chitosan (CTS-MW I), and depolymerized chitosans i.e., (b) CTS-MW II, and (c) CTS-MW III.

From Table 1, it can be seen that the percent DD slightly increase as the amounts of sodium nitrite increase, whereas the M_v and the percent N decrease with an increase in the concentration of sodium nitrite. The percent DD of chitosan presented in Table 1 was derived from the differential volume of NaOH between two inflection points obtained from the 1st derivative potentiometrical plots as shown in Figure 4. From Figure 4 (b) and (c), it can be seen that ΔV of the depolymerized chitosan samples increases with an increase in the amounts of sodium nitrite, indicating that sodium nitrite introduced an additional amine groups into the chitosan backbone. This finding is similar to Seong's report [10]. Therefore, the mechanism of chitosan depolymerization by sodium nitrite is proposed as shown in Figure 5.

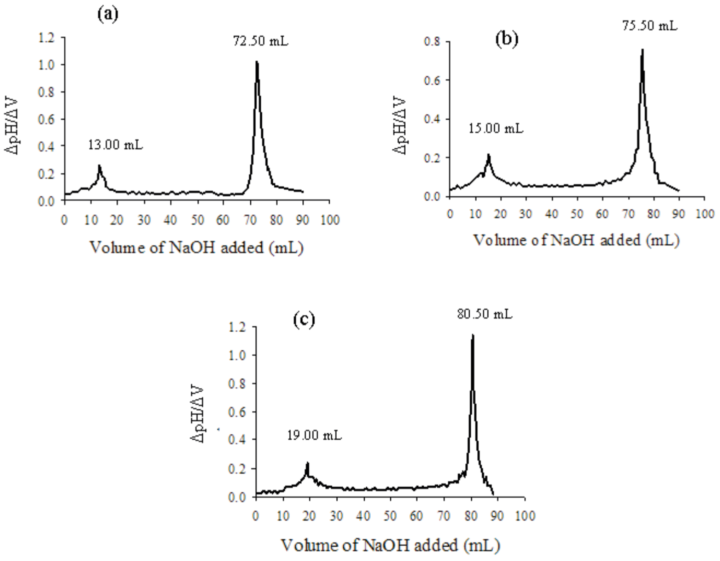


Figure 4. Potentiometric titration of (a) native chitosan ; CTS-MW I ($\Delta V = 59.5\ 10^{-3}$ L), and depolymerised chitosan i.e., (b) CTS-MW II ($\Delta V = 60.5\ 10^{-3}$ L), and (c) CTS-MW III ($\Delta V = 61.5\ 10^{-3}$ L).

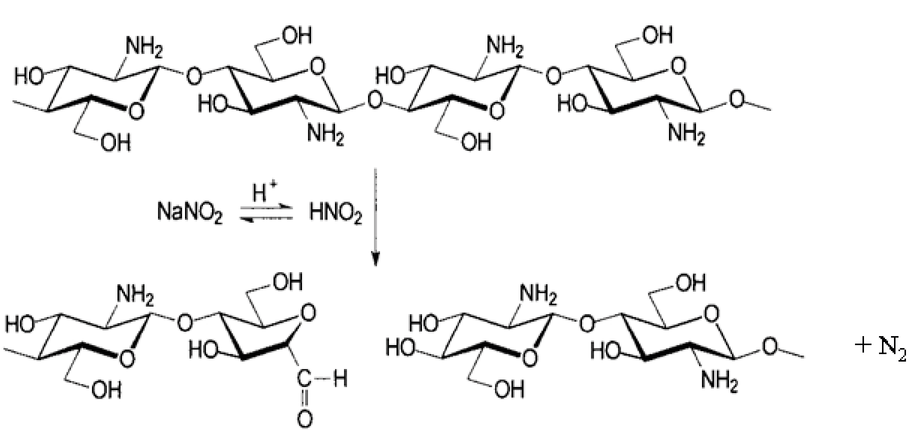


Figure 5. Degradation of chitosan by nitrous acid.

According to Figure 5, sodium nitrite chemically transforms to nitrous acid prior to depolymerization of chitosan polymer chain, resulting in chitosan with low Mw. Following to the depolymerization reaction, the aldehyde end group is also formed, which could act as a reactive group when applied onto cotton fabric. The molecular weight of chitosan and nitrogen content were determined using Eq. (2) and (3), respectively. From Table 1, the products of depolymerized chitosans (as CTS-MW II, and CTS-MW III) have a dramatic decrease in the molecular weight, namely 10.8 and 7 kDa, respectively. However, the nitrogen content was slightly decreased since the weight loss of amine group was relatively small when compared to the molecular weight of chitosan.

3.2 Application of Chitosan onto Cotton Fabrics

Native chitosan and depolymerized chitosans were applied onto cotton fabric. The chitosan present on the fabric surface was indirectly measured via nitrogen determination. The results are showed in Table 2.

Table 2. Percentage of nitrogen content on 1.0 g cotton fabric (n=3).

Chitosan samples	Chitosan conc. (g/L)	N (%) ± SD
Control fabric (scoured fabric)	no chitosan	0.00 ± 0.00
CTS-MW I	2	0.04 ± 0.03
	6	0.12 ± 0.03
	9	0.21 ± 0.05
CTS-MW II	9	0.23 ± 0.08
	19	0.36 ± 0.12
	28	0.94 ± 0.06
	38	0.68 ± 0.09
CTS-MW III	9	0.21 ± 0.06
	19	0.30 ± 0.10
	28	0.57 ± 0.12
	38	0.82 ± 0.30

From Table 2, in all cases, chitosan-fabrics exhibit an increase in percent N with an increase in chitosan concentration. In case of CTS-MW I, an increase in chitosan concentration from 2 to 9 g/L leads to an increase in percent N from 0.04% to 0.21%, respectively. These indicate that the percent N increases with an increase in the chitosan concentration employed. When considering the structure of CTS-MW I, it is likely that CTS-MW I adhered to cellulose solely by physical means. For low Mw chitosans, i.e. CTS-MW II, and CTS-MW III, higher concentrations applied were attainable with no compromise of handling property of chitosan-fabrics. Despite their relatively small Mw, it can be observed that CTS-MW II and CTS-MW III yield relatively higher percent nitrogen contents on the chitosan-fabrics when compared to CTS-MW I. The main reason is that these types of chitosan contain aldehyde functional group generated by nitrite treatment as shown in Figure 4. Therefore, CTS-MW II and CTS-MW III could undergo covalent bonding with cotton cellulose, leading to their adhesion ability. When focused on CTS-MW II, the resultant percent N contents are found slightly higher than those of CTS-MW III. One of the possible reasons is that the affinity of CTS-MW III onto cellulose was lower due to its relatively smaller polymer molecule.

3.3 Effects of Application Methods on Colour Strength

Table 3 shows *K/S* values of the dyed fabric samples treated with chitosans according to the three application methods as mentioned above. In this experiment, two types of chitosans, i.e. CTS-MW I, and CTS-MW III which represent high Mw native chitosan and depolymerized low Mw chitosan, respectively, were compared. The dyeing results show that *K/S* values are dependent on dyeing methods as well as chitosan's molecular weight. In all cases, the optimum *K/S* values are achieved by pre-dyeing method in which the fabrics were treated with chitosan solutions prior to dyeing. In this method, cotton cellulose was pretreated with active chitosans which were adhered to cellulose by hydrogen bonding for native chitosan and covalent bonding for CTS-MW III [11]. The presence of chitosan on cotton fabric was found to enhance the dyeability of treated fabrics as evidenced by an increase in *K/S* values. On the other hand, the post dyeing method seems to produce poor dyeability. It is thought that instead of being absorbed into cellulose to fix the dye molecule the applied chitosan exhibited characteristics in the opposite direction by removing the dye molecule out from the fiber. The resultant chitosan-natural dye complex possessed no affinity to cellulose and subsequently precipitated, resulting in lower colour strength than the control fabric. For the all-in one method, the mixed results are observed. The native chitosan had a tendency to cause dye precipitation through complexation, resulting in poor colour yield. To a lesser extent, CTS-MW III-dye complex was less likely due to its relatively low molecular weight, reflecting the unaffected *K/S* value. In overall, the pre-dyeing method is recommended.

Table 3. Colour strength of dyed chitosan fabrics from three dyeing methods (n=3).

Chitosan samples	**Chitosan conc. (g/L)**	***K/S* ± SD**		
		all-in-one	**pre-dyeing**	**post-dyeing**
CTS-MW I	9	1.04 ± 0.06	2.32 ± 0.16	1.35 ± 0.06
CTS-MW III	38	2.03 ± 0.18	2.26 ± 0.10	1.32 ± 0.00

(The *K/S* ± SD value of control fabric untreated with chitosan was 1.53 ± 0.03.)

3.4 Effects of Chitosan on Colour Fastness And Fabric Stiffness

The colour fastness properties (light and wash fastness) and fabric stiffness obtained from the pre-dyeing method are presented in Table 4. From the table, colour strength is expressed by *K/S* value where the higher the *K/S* value, the stronger the colour strength. It should be noted that *K/S* value of the control fabric in Table 3 (*K/S* = 1.53) is different from those of the control fabric in Table 4 (*K/S* = 2.26) due to a variety of fresh mangosteen leaves as raw materials employed, leading to the variation of the obtained color strengths.

It is found that fabrics treated with chitosan, exhibit an increase in *K/S* values with an increase in percent chitosan coating. This indicates that chitosan is capable of enhancing dyeability of mangosteen dye on cotton fabric. It should be noted that the applied amount of native chitosan was relatively lower than those of depolymerized chitosans due to its high viscosity which caused the undesirable problem of fabric stiffness. In case of depolymerized chitosans, CTS-MW II performs better in promoting the dyeability of treated cotton fabric. This might indicate that the binding sites on CTS-MW II were relatively more than CTS-MW III, resulting in the higher dye immobilization namely arising from chitosan amine group and gallic acid (gallic-COOH) interaction. In this study, the highest *K/S* value of 5.56 was obtained with the applied amount of 28 g/L CTS-MW II. However, it is contradictory that the *K/S* value of 3.34 is obtained lower at 38 g/L CTS-MW II. The obtained result is found in similar manner to the trend of percent N as shown in Table 2. Therefore, it can be said that the *K/S* and percent N results (at 38 g/L CTS-MW II) are not the representative values. As such, it is noted that these values are discarded from discussion.

As mentioned earlier, the native chitosan (CTS-MW I) coating gives the dyeability inferior to depolymerized chitosans. This could also be derived from the phenomenon of surface dyeing, the accumulation of dye on fabric surface. Surface dyeing arose from the formation of chitosan film commonly observed when coated with chitosan having a high molecular weight [8].

Table 4. Properties of dyed fabrics treated with various chitosans.

Chitosan samples	**Chitosan conc. (g/L)**	***K/S***	**Colour changes**		**Stiffness (mm)**	
			Light fastness	**Wash fastness**	**Warp direction**	**Weft direction**
Control fabric	no chitosan	2.26	2	3	23	21
CTS-MW I	2	2.43	2	3	25	20
	6	2.89	2-3	3	21	23
	9	3.60	2	2-3	21	24
CTS-MW II	9	3.88	2-3	3	22	25
	19	4.35	2	3	20	22
	28	5.56	2-3	3-4	21	23
	38	3.34	2	2-3	20	22
CTS-MW III	9	3.72	2	3	21	22
	19	3.44	2	3	21	22
	28	3.63	2	2-3	22	20
	38	4.21	2	3	20	22

Fabric stiffness was assessed by bending stiffness tester. A measured bending length is indicative of fabric stiffness where the higher the bending length, the higher would be the fabric stiffness. The results presented in Table 4 show that all cases of chitosan fabrics exhibit similar stiffness values. For the native chitosan which typically causes fabric stiffness due to its ease of film formation, this problem was minimized by the usage of low concentrations of chitosan solutions (6 to 9 g/L). In the case of depolymerized chitosans, high concentrations (19 to 38 g/L) could be employed without the presence of fabric stiffness thanks to the loss of film characteristic

4. CONCLUSION

In this study, depolymerization of chitosan using sodium nitrite to prepare various low Mw chitosans was carried out. FTIR analysis provided evidence to support that depolymerized chitosan contained an increase in free amine groups as a result of deacetylation of remaining N-acetyl groups. Moreover, the depolymerized chitosan contained an increased percent DD and a decreased percent N with respect to increasing amounts of sodium nitrite. Then, obtained chitosans combined with mangosteen dye extract were applied onto cotton fabric. An effect of chitosan application methods on the properties of dyed fabrics was evaluated. In all cases, the pre-dyeing method in which the fabrics were treated with chitosan solutions prior to dyeing produced the optimum *K/S* value. An increase in chitosan concentration resulted in an increase in the dyeability of mangosteen dye. This effect was associated with the presence of bonded chitosan through the chemical reaction of the chitosan aldehyde group with cellulose. As a result of low Mw employed, depolymerized chitosans with higher concentration (compared to native chitosan) could be employed without the concession of a stiffness problem. The reason for this is due to their low Mw depolymerized chitosans exhibited no film formation.

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