



# Preparation and application of nanochitosan to finishing treatment with anti-microbial and anti-shrinking properties

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## ABSTRACT

In this study, we used low-molecular-weight chitosan (LWCS) to prepare nanochitosan (NCH) and applied this material to wool fabric finishing treatment. The diameters and zeta potential of the nanochitosan decreased as the value of the molecular weight of chitosan decreased. Additionally, the wool fabric was treated with various types of chitosan. The anti-bacterial and shrink-proofing properties of the treated fabric are ranked as following: NCH > LWCS > chitosan. The former two properties also increased as the concentration of nanochitosan increased. In addition, the nanochitosan-treated wool fabric possesses better anti-bacterial and shrink-proofing properties after washing for 20 times.

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## 1. Introduction

Chitosan is the deacetylated product of chitin. Next to cellulose, chitin is the second most abundant polysaccharide in nature (Rathke & Hudson, 1994). Chitosan has been used in a very wide range of applications, such as prevention of water pollution by chelating heavy metals or radioactive isotopes; in membrane separation (Aiba, Izume, Minoura, & Fujiwara, 1986); in medicine and biotechnology; and in the food areas, either as a food packaging material because of its anti-bacterial action (Ghaouth, Arul, & Ponnampalalan, 1991; Ghaouth, Arul, Ponnampalalan, & Boulet, 1991; Wong, Gastineau, Gregorski, Tillin, & Pavlath, 1992) or as dietary fiber and a potential medicine against hypertension thanks to its scavenging action for chloride ions (Ishikura, 1993; Muzzarelli, 1996; Okuda, 1995).

Nanochitosan is a natural material with excellent physicochemical properties. It is environmentally friendly and bioactive. It is frequently used as a controlled-release drug carrier for gene transfer in artificial organs and for immune prophylaxis. In addition, nanochitosan has been used to improve the strength and washability of textiles and to confer anti-bacterial effects (Ting & Shen, 2005). Nanochitosan can be prepared in several ways. (Berthold, Cremer, & Kreuter, 1996) initially prepared chitosan particles using sodium sulphate as the precipitation agent. Tian and Groves (1999) improved this technique and obtained 600–800 nm chitosan nanoparticles. In 1994, Ohya, Shiratani, Kobayashi, and Ouchi (1994) used glutaraldehyde as a cross-linking agent to cross-link the free amino groups of

chitosan; then emulsified using W/O emulsifier, producing 5-fluorouracil (5-FU) chitosan particles (average particle size:  $0.8 \pm 0.1 \mu\text{m}$ ). In 1989, Bodmeier, Oh, and Prammar (1989) first applied the ionic cross-linking method to prepare chitosan nanoparticles. Tokumitsu et al. reported that it was easy to incorporate drugs in chitosan solution by adding an emulsifier and agitating at high speed to produce  $426 \pm 28 \text{ nm}$  chitosan nanoparticles. (Janes, Fresneau, & Marazuela, 2001; Tokumitsu, Ichikawa, & Fukumori, 1999) Although several studies have prepared nanochitosan from low-molecular-weight chitosan (LWCS), none have investigated the effects of its molecular weight on the nanochitosan particle size and zeta potential. In our previous research papers (Huang, Wu, Chen, & Lian, 2008), we showed that LWCS treatment provides good anti-wrinkle to cotton. LWCS shows a better effect than non-degraded chitosan. It is due to better osmosis by reducing molecular weight. So, in the study, we degraded chitosan into LWCS, then produced nanochitosan. Then, wool fabric was treated by various types of chitosan again. We first studied the effects of LWCS's molecular weight on the nanochitosan particle size and zeta potential, secondly studied the effects of chitosan type and nanochitosan concentrations on the anti-bacterial and shrink-proofing properties of the wool fabric.

## 2. Experimental

### 2.1. Materials

Ethanol, acetic acid, HCl,  $\text{H}_2\text{O}_2$  and sodium tripolyphosphate (TPP) were all reagent grade and purchased from Shimadzu Medicine

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(Osaka, Japan). The chitosan (85% deacetylated;  $M_v = 240,500$ ) was supplied by Taiwan Kaohsiung Applied Chemistry (Kaohsiung, Taiwan). The wool fabrics used as test products were pretreated by the washing and grabbing process. They were supplied by Shun Fu Yai Industrial Co., Ltd. [48Nw  $\times$  48Nw, ends (52) and picks (44); 66-inch width].

## 2.2. Methods

### 2.2.1. Preparation of nanochitosan

Two grams of chitosan were dissolved in 100 ml 0.1 M HCl and stirred for 30 min. Then,  $H_2O_2$  was added in one of five concentrations (2.5%, 5%, 10%, or 15%). The mixture was heated and stirred at 60 °C for 2 h and then vacuum filtered. The upper residue was neutralised with distilled water, baked, and weighed. Ethanol was added to the lower solution, which was left for 24 h to precipitate, after which it was filtered, dried, and weighed. This gave low-molecular-weight water-soluble chitosans denoted by C2.5, C5, C10, and C15. After  $H_2O_2$  treatment, the molecular weight of the chitosan decreased and continued to decrease as more  $H_2O_2$  was added (Table 1). This was due to the degradation of the chitosan molecular chain by  $H_2O_2$  (Huang, Wu, Chen, & Lian, 2008).

Then, 0.5 g of LWCS was dissolved in 1L of 2% acetic acid and stirred for 30 min. Then, 100 ml of each solution was added to 40 ml of TPP (0.2, 0.4, 0.5, or 1.0 g/L), stirred for 2 h at ambient temperature and then centrifuged at high speed. The isolated nanochitosan was rinsed with distilled water, freeze-dried and analysed. These samples were denoted N-Cn (N-C5, N-C10 and N-C15), respectively.

### 2.2.2. Finishing process of wool fabric with nanochitosan

About 0.5–2 g N-Cn was dissolved into 200 ml (2%) acetic acid solution and stirred until complete dissolution. Wool fabric were dipped into the N-Cn solution for 5 min by 2 dips 2 nips process (to soak twice (5 mins/each time), with a pressing step after each soaking), pick-up about 90%, under 80 °C, pre-dry 5 min, and then curing for 3 min under 100 °C. Then the properties of the treated wool fabric were tested.

### 2.2.3. Analysis of LWCS and nanochitosan

The particle size distribution and zeta potential of the chitosan nanoparticles were determined using a Zetasizer 3000HSA (Malvern Instruments, Southborough, MA, USA). The treated fabrics were measured for their shrink-proofing property according to the AATCC TM 187-2001 method. The anti-bacterial properties of the samples were tested according to method JIS1902-1998 of the Japanese Association for the Functional Evaluation of Textiles (JAFET). The following equations were used to calculate the bacterial growth, bacteriostatic and bactericidal values:

$$\text{Bacterial growth}(F) = \log(M_b/M_a) \quad (1)$$

An  $F$  value  $>1.5$  indicated statistical significance in the experiment.

$$\text{Bacteriostatic value}(S) = \log(M_b/M_c) \quad (2)$$

An  $S$  value  $>2.2$  suggested that the sample had a bacteriostatic effect.

$$\text{Bactericidal value}(L) = \log(M_a/M_c) \quad (3)$$

An  $L$  value  $>0$  suggested that the sample had a bactericidal effect.  $M_a$  was the bacterial number in the sample of un-pretreating fabrics immediately after rinsing.  $M_b$  was the bacterial number in the sample of un-pretreating fabrics after culturing for 18–24 h.  $M_c$  was the bacterial number in the sample of the pretreatment fabrics after culturing for 18–24 h.

Investigations on the leaching behaviour were performed at 40 °C using a Rapid H-type dyeing machine. As washing solution an 1% aqueous solution of sodium lauryl sulfate SDS with pH 7 was used. After a leaching 20 min the textile samples were rinsed intensively with water, dried at room temperature and physical properties again investigated after washing 20 times.

## 3. Results and discussion

### 3.1. Particle size

Some experts pointed out that the concentrations of the LWCS and TPP solutions and the ratio of LWCS to TPP by weight have important effects on nanochitosan preparation (Bodmeier, Chen, & Paeratalml, 1989). Table 1 shows the effect of the LWCS molecular weight on the nanometric LWCS–TPP particle size: The lower the LWCS molecular weight, the smaller the particles derived from the chitosan and TPP reaction (Wu, Chen, & Huang, 2005). These results indicate that the formation of nanoparticles depended dramatically on the concentration of free amino groups, which increased the surface charge and zeta potential of the nanoparticles and strengthened the electrostatic interactions between the chitosan and the TPP, helping to reduce the particle sizes (Yang & Hon, 2009). Fig. 1A shows the particle size distribution curve of nanochitosan made from C10. A single peak occurred in the particle size distribution, indicating excellent uniformity.

### 3.2. Zeta potential

From Table 1, the zeta potential decreased gradually with the incorporation of TPP. After the TPP solution was added, the positive charge on the chitosan particle surface was neutralised by the negative charge on the phosphate group. This was reduced gradually as intermolecular and intermolecular cross-links formed between the TPP groups and LWCS amino groups. The optimum cross-linking occurred when the mass ratio of LWCS/TPP was approximately 5:2, at which the measured zeta potential was also minimal at 7.8. Table 2 shows the effects of the molecular weight of LWCS on the nanochitosan zeta potential: The zeta potential decreased with the LWCS molecular weight. Fig. 1B shows the potential curve of nanochitosan made from C10; again the potential distribution has a single peak, indicating excellent uniformity.

### 3.3. Effect on the anti-bacterial and shrink-proof properties of fabrics

The amine groups of chitosan can become changed under weak acid condition into the  $-NH_3^+$  anion, which can interact with the cell wall of bacteria and hinder the growth of the microorganism (Zheng & Zhu, 2003). Table 2 shows that the anti-bacterial property of treated fabrics is better than that of the untreated fabric, espe-

**Table 1**

Effect of molecular weight of LWCS on the particle size and zeta potential of nanochitosan.<sup>a</sup>

M.W. of LWCS <sup>b</sup>	Conc. of TPP (mg ml <sup>-1</sup> )							
	0.2	0.4	0.5	1.0	0.2	0.4	0.5	1.0
	Particle size (nm)				Zeta potential (mV)			
240,500 <sup>c</sup> (C0)	597.6	176.7	134.4	223.2	51.0	39.3	33.5	15.5
120,250 (C2.5)	523.7	132.9	98.3	148.1	42.3	32.8	27.3	14.0
77,210 (C5)	453.9	106.8	81.0	119.5	37.5	28.4	22.4	13.3
15,090 (C10)	436.7	84.0	67.0	95.9	35.7	27.8	17.3	12.0
3650 (C15)	235.0	71.5	55.3	84.1	27.9	17.9	15.0	11.8

<sup>a</sup> Volume of CS and TPP were 100 ml and 40 ml.

<sup>b</sup> Concentration of LWCS is 0.5 (mg ml<sup>-1</sup>).

<sup>c</sup> Chitosan.

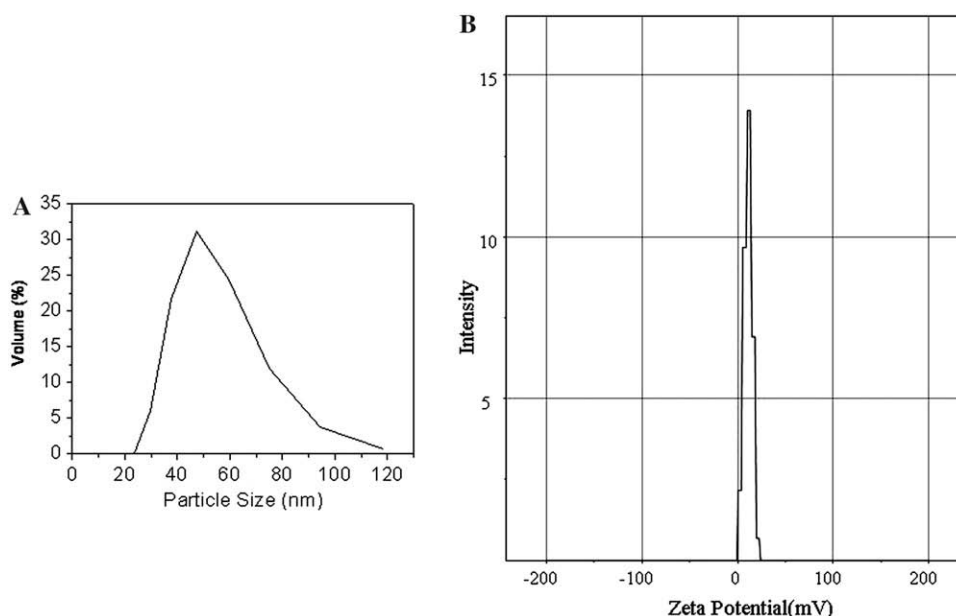


Fig. 1. The particle size distribution and zeta potential of nanochitosan (N-C10) (A, size distribution; B, zeta potential).

**Table 2**  
The anti-bacterial and shrinkage properties of treated fabrics.

Finishing reagents	N-Cn conc. (%)	Anti-bacterial property		Shrinkage (%)	
		Bacteriostatic value	Bactericidal value	Warp	Weft
Control <sup>a</sup>		4.2	2.2	6.6	5.4
0 <sup>b</sup>		0	<0	11.7	8.6
LWCS <sup>c</sup>	0.25	4.4	2.3	6.4	5.2
N-C5		4.8	2.3	6.1	5.1
N-C10		5.0	2.4	5.4	4.9
N-C15		5.2	2.7	5.0	4.8
N-C10	0.25	5.0	2.4	5.4	4.9
	0.50	5.1	2.7	4.8	4.2
	1.00	5.3	3.0	4.0	3.7

<sup>a</sup> Treated with chitosan.

<sup>b</sup> Greige fabric.

<sup>c</sup> Treated with LWCS (C10).

cially after treatment with N-Ca. This is because the molecular weight of LWCS is low and so the osmosis effect is strong. The anti-bacterial property of treated fabrics was improved with the reduction of the molecular weight of LWCS and with the increase in the concentration of N-Cn. Some previous studies on the effect of chitosan on wool fabric were available. TWool fabrics have been treated with chitosan/protease which improved the performance

of shrink-proof of wool and the shrink-proof rate by 7.3% (Zhang, 2008). Also, Guo et al. described the addition of sodium tripolyphosphate (TPP) and showed that this can enhance the amount of adsorption of the chitosan increasing shrink reduction and anti-bacterial activity. They found that at a chitosan concentration of 2 g/L and TPP concentration of 1.5 g/L, the fabric shrink-proof rate increased by 3–10%, and the bacteriostasis for *Escherichia coli* by 74.7% (Guo, Huang, & Cong, 2008). The results showed that the nanoparticles size of finishing agent can enhance the effect of the wool fabric.

The shrinkage of the untreated fabrics in both the warp and the weft direction is larger than that of the treated fabrics, as shown in Table 2. This result is because the yarn of the untreated fabrics is stretched taut during weaving, whereas the treated fabrics have reactive polymers completely covering the fiber scales or an even layer of protective thin membrane formed over the surface. In turn, the latter would make the tightness of the yarn, the structure of the fabric, and weaving density more restrictive to the movement of individual fibers. Under such circumstances, the fibers in the treated fabric would, of course, become much more resistant to outside forces and not glide against each other; that is, the fabric would become more shrink-proof (Liu, 1997). Therefore, when the osmosis of chitosan in fabric is better, the area covered by chitosan on the surface of the fiber becomes larger. Nanochitosan-treated fabric has better shrink-proofing properties. It was noticed also that

**Table 3**  
Washing fastness of treated fabric.

Samples	Before washing				After washing 20 times			
	Anti-bacterial		Shrinkage (%)		Anti-bacterial		Shrinkage (%)	
	A <sup>d</sup>	B <sup>e</sup>	Warp	Weft	A <sup>d</sup>	B <sup>e</sup>	Warp	Weft
0 <sup>a</sup>	0	<0	11.7	8.6	0	<0	13.6	9.7
N-C10 <sup>b</sup>	5.3	3.0	4.0	3.7	4.6	2.7	4.4	4.2
Control <sup>c</sup>	4.2	2.2	6.6	5.4	3.0	1.8	7.4	6.3

<sup>a</sup> Untreated fabric.

<sup>b</sup> Concentration is 1.0%.

<sup>c</sup> Treated with chitosan.

<sup>d</sup> Bacteriostatic value.

<sup>e</sup> Bactericidal value.

shrinkage in the warp direction was always greater than that in the weft direction. This difference is because the warp yarn is stretched more tightly than the weft yarn during weaving, which is also the main reason why woollen fabrics are prone to shrink when heated. The shrink-proofing of treated fabrics is improved with the reduction of the molecular weight of LWCS and with increase in the concentration of N-Cn.

### 3.4. Wash fastness

Table 3 shows the anti-bacterial and shrink-proof properties fastness of treated fabrics after they had been washed 20 times. The fastness of the untreated fabric was very poor. The treated fabric with N-C10 preserves shrink-proofing and anti-bacterial properties after washing better than the control. This is because the particle size of the nanochitosan is smaller and its osmosis is higher making it more difficult to wash out.

## 4. Conclusions

In this study, we degraded chitosan into LWCS, then produced nanochitosan (NCH). The wool fabric was treated with the various types of chitosan. The anti-bacterial and shrink-proofing properties of the treated fabric are ranked as following: NCH > LWCS > chitosan. The former two properties also increased as the concentration of nanochitosan increased. In addition, the nanochitosan-treated wool fabric is able to provide better anti-bacterial and shrink-proofing properties after washing 20 times.

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