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Microwave-assisted antimicrobial finishing of wool fabric with chitosan derivative

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Chitosan guanidine hydrochloride derivative has been synthesized by the guanidinylation reaction of chitosan with thiourea trioxide. The structures of chitosan guanidine hydrochloride are characterized by FTIR and ^{13}CNMR. A microwave heating system has been used to apply chitosan guanidine hydrochloride on wool fabric to impart antimicrobial finishing. Conventional and microwave-assisted finishing of wool fabric with chitosan guanidine hydrochloride is compared. The influence of microwave heating on the efficiency of crosslinking is studied by SEM and FTIR. Scanning electron microscopy substantiates adhesion of the chitosan guanidine hydrochloride on the surface of the wool under microwave heating. Microwave-based finished samples show better antimicrobial properties and durability after 40 washes than conventionally finished samples without losses in strength properties.

Keywords: Antimicrobial finishing, Guanidinylated chitosan, Microwave heating, Wool

1 Introduction

The ability of a substrate to absorb microwave energy is determined by its polarity. When an electrical field is applied at microwave frequencies, the polar molecules rotate in an attempt to rearrange their dipole moment with the changing electrical field. Energy is absorbed and heat is generated by the internal friction between the rotating molecules[1]. In recent years, some new techniques and methods have been studied for saving energy and ecofriendly textile processing. The use of microwave heating method in textile dyeing and finishing has been the subject of considerable importance because of various advantages such as uniformity, flexibility, less energy and high efficiency [2-7].

Wool has been widely used as a high-quality textile material, such as suiting, carpet, blankets and shawls due to its good elasticity, flexibility, wettability, biodegradability and biocompatibility. Compared with other natural fibre, wool has a relatively higher dielectric constant (ε) and so microwave irradiation can generate heat on wool fibre through non-contact heating. The use of high efficient microwave heating method in wool dyeing and finishing to achieve energy savings and high efficiency has been the subject of considerable interest[8-11].

Chitosan has biodegradability, biocompatibility and environment-friendly nature. It also has a complex double-helix structure including –OH and -NH_2 groups with strong reactivity, which helps in carrying out a variety of chemical modification under appropriate conditions, to improve its solubility. Guanidinium salts have increased interest in recent years. Their derivatives with antimicrobial and antifungal activity have been investigated as medical and crop protection agents and antiseptics for industry products, food and daily necessities[12]. Guanidinylation of chitosan can not only enhance the water solubility of the chitosan, but also improve the stability of low molecular weight guanidine salt; guanidinylated chitosan treated wool fabrics show significantly improved antimicrobial characteristics[13]. Textile finishing using microwave heating has been reported by several authors[10,14,15] and the result showed that microwave treatment can obtain clean, environment-friendly and highly efficient heating effect in textile finishing process. The use of microwave-assisted heating for antimicrobial finishing with citric acid and chitosan guanidine hydrochloride has not been reported in the published literature.

A water-soluble guanidinylated chitosan derivative, namely chitosan guanidine hydrochloride (CGH) has been synthesized (Fig. 1), and then characterized by FTIR and ^{13}CNMR. The aim of this study is to investigate the effect of microwave heating on the antimicrobial properties of wool fabrics treated with citric acid and chitosan guanidine hydrochloride in comparison with conventionally finished wool fabric.

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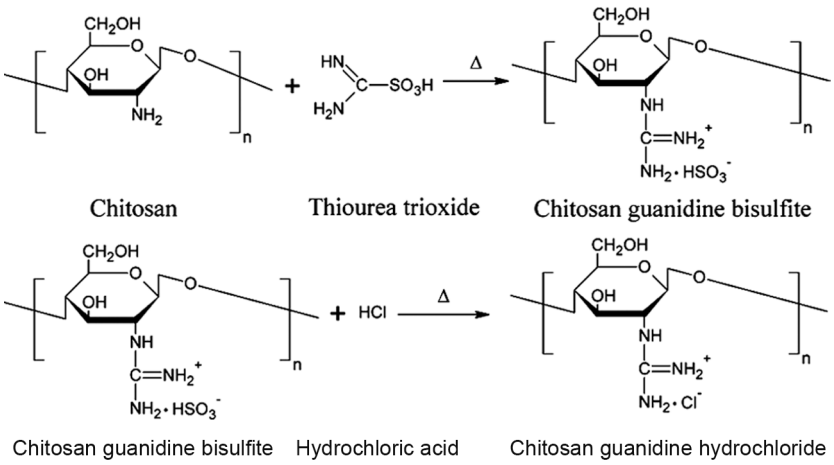

Fig. 1—Synthesis of chitosan guanidine hydrochloride (CGH)

2 Materials and Methods

2.1 Materials

100% wool fabric (Shandong, China) with the specifications 23S/2×22S/2 97×61 was used. Chitosan (molecular weight 800 KDa; the degree of deacetylation 96.0%), sodium silicate, beef extract, agar and peptone were supplied by Guoyao Chemical Reagent Co. Ltd (Shanghai, China). Hydrochloric acid was supplied by Pinghu Chemical Reagent Co. Ltd (Shanghai, China). Thiourea trioxide was supplied by Beihong Chemical Reagent Co. Ltd (Tianjin, China). Hydrogen peroxide (30%) was supplied by Jinlu Chemical Reagent Co. Ltd (Shanghai, China). Citric acid and sodium hydroxide were supplied by Yijia Chemical Reagent Co. Ltd (Shanghai, China). *E.coli* and *S.aureus* were supplied by Donghua University (Shanghai, China)

2.2 Preparation of Chitosan Guanidine Hydrochloride

Chitosan (4.5g) was dissolved in 0.05moL/L hydrochloric acid followed by the addition of thiourea trioxide (3.9g). The mix was then kept at 50°C for 60min. The desired amount of hydrochloric acid (corresponding to a molar ratio of 1:1 compared with chitosan residue) was added and solution was kept at 50°C for another 3h, after that solution was cooled to room temperature. The mixture was washed thoroughly with ethanol, and then dried under vacuum to obtain the final product (Fig.1).

2.3 Fabrics Treatment

Prior to antimicrobial treatment, all wool fabrics were pretreated at 70 °C for 1h in baths containing 2g/L of sodium silicate and 18g/L of hydrogen peroxide (30%), maintaining 30:1 liquor-to-goods ratio and 9 *p*H, the contents were finally rinsed in distilled water and air dried.

After oxidation pretreatment, the wool fabrics were padded with two dips and nips (70% wet pick up) in a solution containing chitosan guanidine hydrochloride (20%, owf), citric acid CA (20%, owf) and hypophosphite (20%, owf). Immediately after padding, half of the samples was simultaneously heated at 700W power for 2 min in the microwave chamber [microwave oven(Yk-01) used in this study has continuous adjustable power of 250-1000W]. The other half of the fabric samples was dried at 80°C for 5 min, and cured at 130°C for 5 min. After heating, the fabric was then thoroughly rinsed with hot water at 50°C and air dried in a standard atmosphere for testing (20±1°C and 65±2RH).

2.4 Testing and Analysis

For measurement of minimal inhibition concentration, chitosan guanidine hydrochloride solutions (0.6, 0.8, 1.0, 1.2, 1.4 mg/mL) were heated at 45°C and poured into autoclaved petri-dishes, cooled, one loopful of microorganism suspension was spread on cooled nutrient agar, then incubated at 37°C for 24h. The MIC is defined as the lowest concentration of the tested sample at which the microorganism colonies are not visible with naked eye.

The antimicrobial test was carried out according to the antimicrobial standard of the Japan Association for the Evaluation of Textile and JIS L1902-2002 test method (adsorption method). The durability of the treated wool fabric against repeated launderings was evaluated by washing wool fabrics according to AATCC test method 61-2A. The breaking strength of the fabric was measured according to ASTMD

5034 test method. CIE whiteness was evaluated using a Datacolor SF650 color measuring and matching instrument (Datacolor Ltd, USA). SEM analysis was done on JEOL JSM-5600LV machine (JEOL Ltd, Japan). Infrared (IR) spectra were recorded on a Nicolet NEXUS-670 Infrared spectrophotometer (Nicolet Ltd, USA). Adsorption rate of chitosan guanidine hydrochloride on wool was estimated by measuring the changes in the dry weights of the sample, as shown below:

$$\text{Absorption rate}(\%) = \frac{\text{Dry wt after treatment} - \text{Dry wt before treatment}}{\text{Dry wt before treatment}} \times 100$$

3 Results and Discussion

3.1 Characterization of Chitosan Guanidine Hydrochloride

Fourier transform-infrared spectroscopy and ^{13}CNMR analyses indicate the success of the guanidylation reaction. Figure 2 shows the IR spectra of chitosan and chitosan guanidine hydrochloride.

The IR spectra of chitosan guanidine hydrochloride show a new beak at 1637cm^{-1} assigned to the stretching vibration of C=NH in guanidine group [-HNC(=NH)NH$_2$] and the peak at 1601cm^{-1} assigned for binding vibration of –NH$_2$ group of chitosan gets disappear. The new stronger peak at 1085 cm^{-1} is assigned to the stretching vibration of C-N-C and the peak at 1323cm^{-1} is assigned to the stretching vibration of C-N. In addition, the new stronger peaks at 1384cm^{-1} and 1532 cm^{-1} also have confirmed the role of guanidinylation. The ^{13}CNMR spectra of chitosan and chitosan guanidine hydrochloride in HCl/D$_2$O are shown in Fig. 3.

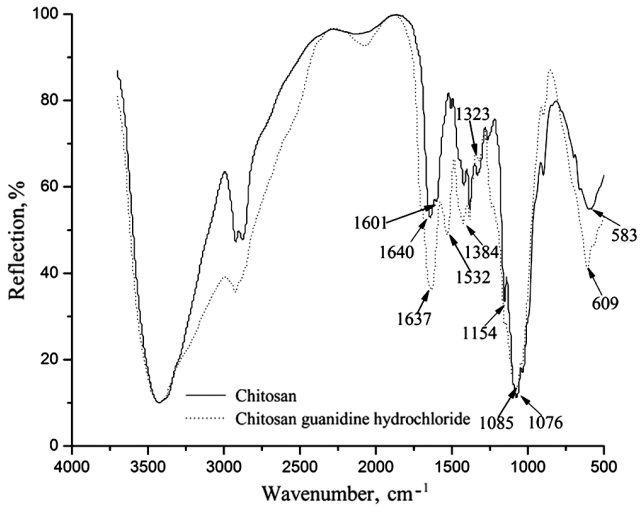

Fig. 2—FTIR spectra of chitosan and chitosan guanidine hydrochloride

Comparing the ^{13}CNMR spectrum of chitosan with that of chitosan guanidine hydrochloride, the distinct signals at 158.3 ppm are assigned to the carbon of guanidine groups, and the ^{13}CNMR chemical shifts for chitosan at 58.6(C2), 62.7(C6), 72.8(C3), 77.3(C5), 79.0(C4) and 100.1(C1) (ppm) are detected. In contrast to chitosan, the signals of chitosan guanidine hydrochloride at 58.6(C2), 62.7(C6), 72.8(C3), 77.3(C5), 79.0(C4) and 100.1(C1) (ppm) are attributed to the polysaccharide structures. The ^{13}CNMR spectra confirm that the amino groups of chitosan are partly guanidinylated.

3.2 Measurement of Minimal Inhibition Concentration

Antimicrobial activity of chitosan guanidine hydrochloride against *E.coli* and *S.aureus* is shown in Fig. 4.

Figure 4 shows that minimal inhibition concentration of chitosan guanidine hydrochloride against *E.coli* and *S.aureus* are 1.4 mg/mL and 1.2 mg/mL. Guanidinylated chitosan has better antimicrobial activity against *S.aureus* [16,17].

3.3 Comparison between Microwave and Conventional Heating

The physical properties and adsorption rate of microwave and conventional heated samples are given in Table 1.

Table 1 shows that the use of the microwave heating system effectively reduces the drying and

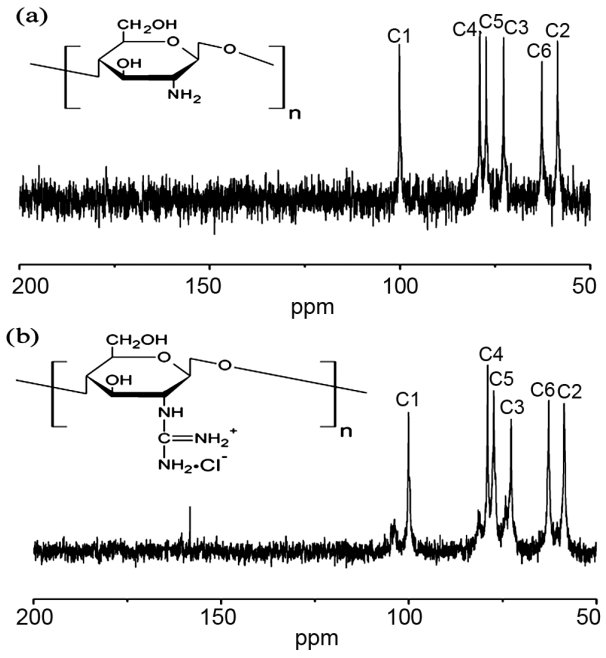

Fig. 3—^{3}CNMR spectra of (a) chitosan and (b) chitosan guanidine hydrochloride

curing time as compared to the conventional drying and curing system. The microwave-heated sample shows a significant improvement in whiteness and adsorption capacity at 700W power for 2min when compared with the conventionally heated sample. Retentions of breaking strength of microwave-heated sample and conventionally heated sample are higher than untreated sample. Retention of breaking strength with conventionally heated sample is found slightly higher than microwave-heated sample. The microwave-heated sample shows higher uniformly and degree of crosslinking as compared to conventionally cured sample. As a consequence, a uniform distribution of crosslinks occurs throughout the microstructure which prevents serious losses in strength[14].

3.4 FTIR Analysis

Figure 5 shows that for wool oxidized and treated with CGH or CA and CGH, at 1042 cm^{-1} there is S-O contraction which is increased by oxidation; at 1170 cm^{-1} and 1176 cm^{-1}, there is C-O contraction; at 1706 cm^{-1}, there is C=O contraction; at 1239 cm^{-1}, there is C-N contraction, which is found obvious as compared to untreated wool. The -COOH group of CA, and –OH and -NH_2 groups of wool fibre and chitosan guanidine hydrochloride become –COO- and –CONH-[18,19], indicating that there is an increase in crosslinking after oxidation. The increase in absorbance at 1170, 1176 and 1706 cm^{-1} is higher for microwave-heated samples as compared to that for conventionally heated sample. This indicates that there are more hydroxyl groups associated with crosslinking bond formation, for microwave-heated sample as compared to that for the conventionally heated sample.

Table 1—IE whiteness and breaking strength of wool oxidized and treated with CGH

[Whiteness – 10.86 (untreated); and tensile strengths (Wrap)– 834.8N (untreated) and 823.2N (pretreated) wool fabrics]

Heating system	CIE whiteness	Strength (warp) N	Adsorption rate %
Microwave (without CA)	29.61	892.7	2.22
Conventional (without CA)	22.86	905.2	1.36
Microwave (with CA)	23.41	918.7	-
Conventional (with CA)	20.54	950.0	-

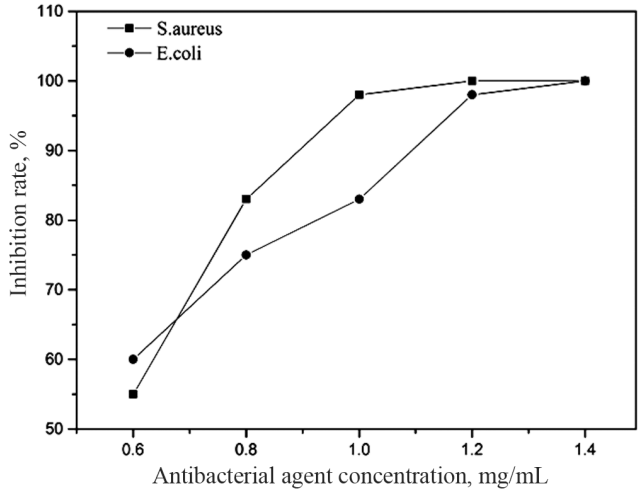

Fig.4—Antimicrobial activity of CGH against *E.coli* and *S.aureus*

3.5 SEM Analysis

Compared to Figs 6 (a) and (b), Figs 6 (c) and (d) show a relatively smoother surface substantiated adhesion of the chitosan guanidine hydrochloride on the surface of the wool under microwave heating.

3.6 Antimicrobial and Wash Fastness Analysis

Oxidized wool was treated with chitosan guanidine hydrochloride or CA and chitosan guanidine hydrochloride under conventional heating and microwave heating and then wash-tested multiple times according to AATCC test method 61-2A. The antimicrobial (against *S.aureus*) and wash fastness results are given in Table 2.

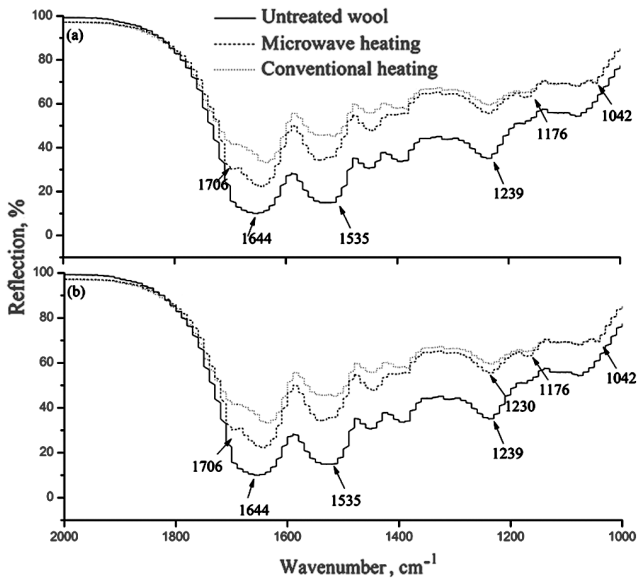

Fig.5—FTIR spectra of untreated wool, wool oxidized and treated with CGH (a), and that oxidized and treated with CGH and CA (b)

Table 2—ntimicrobial activity and durability of wool oxidized and treated with CGH

[Bacterial growth activity value is 2.0. Average common logarithm for the number of bacteria, obtained from three standard samples after 18 h incubation is 6.7]

Wash number	Number of bacteria, CFU/mL				Bacteriostatic value			
	Microwave heating		Conventional heating		Microwave heating		Conventional heating	
	Without CA	With CA	Without CA	With CA	Without CA	With CA	Without CA	With CA
0	0	0	0	0	6.7	6.7	6.7	6.7
10	2.6×10^4	1.3×10^3	3.8×10^4	2.0×10^3	2.3	3.6	2.1	3.4
20	4.8×10^4	2.6×10^3	5.9×10^4	3.9×10^3	2.0	3.3	1.9	3.1
40	2.1×10^5	2.5×10^4	2.5×10^5	3.2×10^4	1.4	2.3	1.3	2.2

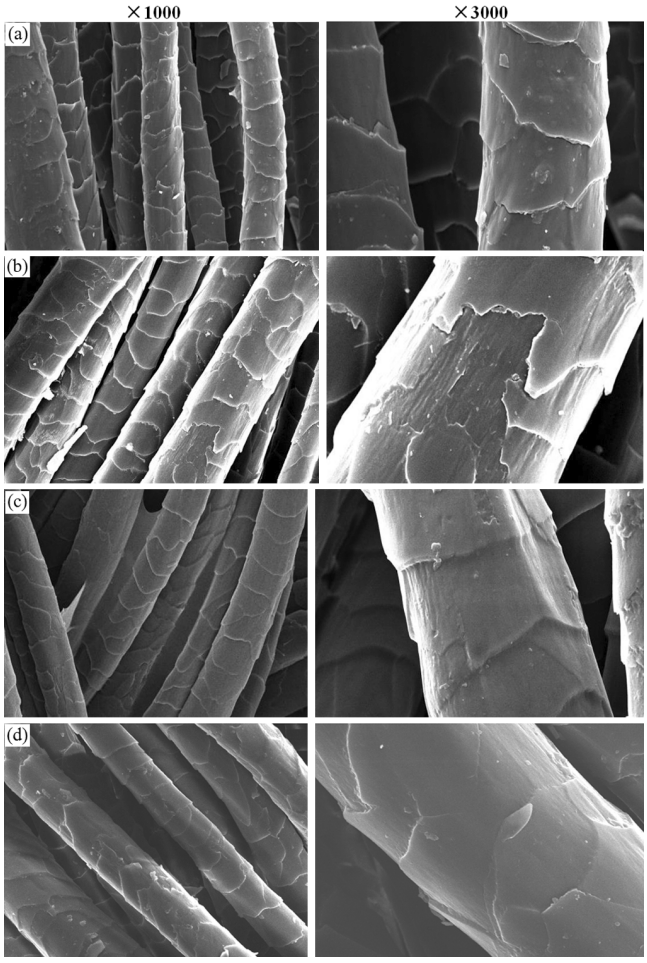

Fig.6—SEM photographs of untreated wool (a), wool oxidized with hydrogen peroxide (b), wool oxidized and treated with CGH (c), and wool oxidized and treated with CGH and CA (d)

Table 2 shows that when CA is added after 40 washings in microwave-heated sample, the number of bacteria is 2.5×10^4 & bacteriostatic value is 2.3, and in conventionally heated sample number of bacteria is 3.2×10^4 & bacteriostatic value is 2.2, which maintains decent antimicrobial properties, revealing a good crosslinking effect under both microwave and conventional heating. Microwave heating for 2 min exhibits slightly higher antimicrobial activity than conventional heating for 10 min. The use of the microwave heating system reduces the drying and curing time as compared to the conventional system and effectively decreases the number of bacteria after multiple washings. It can be summarized that microwave irradiation treatment technique has significant potential for antimicrobial finishing of wool fabric as microwave is a clean, environment-friendly and highly efficient heating technology.

4 Conclusion

Chitosan guanidine hydrochloride with good water solubility has been prepared by the guanidinylation reaction of chitosan with thiourea trioxide. Chitosan and chitosan guanidine hydrochloride are characterized by means of FTIR and ^{13}CNMR, and it is conformed that the guanidine group is introduced into chitosan main chains. Guanidinylated chitosan has good antimicrobial activity against *E.coli* and *S.aureus*. Treatment of wool fabric with chitosan guanidine hydrochloride using conventional and microwave heating techniques is investigated. Scanning electron microscopy supports the adhesion of the chitosan guanidine hydrochloride on the surface of the wool under microwave heating. Microwave-heated samples show slightly higher degree of crosslinking, antimicrobial properties and durability (40 washes) than conventionally heated samples without high losses in strength properties.

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References

1 Montazer M, *Text Chem Color*, 11(1)(2004) 23.

2 Al-Mousawi S M, El-Apasery M A & Elnagdi M H, *Molecules,* 18 (9) (2013)11033.

3 Haggag K, El-Sayed H & Allam O G, *Natural Fibers*, 4(3)(2007) 1.

4 Öner E, Büyükakinci Y & Sökmen N, *Color Technol*, 129(2) (2013)125.

5 Yoshimura Yurika, *Seni Gakkaishi*, 63(6)(2007)146.

6 Lei N N, Gong D L & Ling X R, *Adv Mates Res*, 627(12)(2012) 343.

7 Hou A Q, Wang X J & Wu L H, *Carbohydr Polym*, 74(4)(2008)934.

8 Zhao X & He J X, *Indian J Fibre Text Res*, 36(3)(2011)58.

9 Zhao X & He J X, *J Appl Polym Sci*, 119(2)(2011)944.

10 Zhao S, Ding Y Q & Yu Q C, *Appl Mech Mater*, 184-185(6)(2012)1442.

11 Delaney M J, *Text Chem Color*, 4(5)(1971)29.

12 Qian L Y, Guan Y, He B H & Xiao H N, *Polymer*, 49(10)(2008) 2471.

13 Zhao X, Qiao Z Z & He J X, *J Eng Fiber Fabric*, 5(3)(2010)16.

14 Fouda M M G, El Shafei A, Sharaf S & Hebeish A, *Carbohydr Polym*, 77(3)(2009)651.

15 Purwar R & Joshi M, *Text Chem Color*, 5(11)(2005)41.

16 Hu Y, Du Y M, Yang J H, Kennedy J F, Wang X H & Wang L S, *Carbohydr Polym*, 67(1)(2007)66.

17 Zhao X, He J X & Zhan Y Z, *Polym J*, 41 (12) (2009) 1030.

18 Jeong Y J, Cha S Y, Yu W R & Park W H, *Text Res J*, 72(1)(2002)70.

19 Church J S, Corino G L & Woodhead A L, *Biopolymer*, 42(1)(1997)7.