

***N*-Acyl Chitosan and Its Fiber with Excellent Moisture Absorbability and Retentivity: Preparation in a Novel [Gly]Cl/Water Homogeneous System**

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ABSTRACT: *N*-acyl chitosans (such as *N*-acetylated, *N*-maleyl, and *N*-succinyl chitosan), which were synthesized in glycine chloride ([Gly]Cl)/water homogeneous system, were of better moisture-absorption and moisture-retention abilities than those from the traditional methods, even better than hyaluronic acid. Moreover, the new method overcame many shortcomings, such as long reaction time, gel formed during the process of reaction, and complex workup procedure. In addition, the new [Gly]Cl solvent system was of the low volatility and no corrosion compared with organic solvent, especially, could be repeatedly used. Therefore, an environmental friendly approach for the synthesis of *N*-acyl chitosan was provided. At the same time, the *N*-acetylated chitosan fibers by wet-spinning using *N*-acetylated chitosan-[Gly]Cl as spinning dope solution were firstly reported, and the fibers had smooth surface as well as round and compact structure. More to the point, the *N*-acetylated chitosan fibers directly prepared in this study were of excellent mechanical properties. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3282–3289, 2013

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INTRODUCTION

N-acyl chitosan and its derivatives, a group of fatty or aromatic acyl macromolecular compounds, are of great interest due to their excellent water solubility and biodegradability,¹ thus have been widely used in cosmetics, pharmaceuticals, personal care, and household products. In particular, *N*-acyl chitosan has also been studied as an ideal substitute for HA (hyaluronic acid) because of its favorable hygroscopicity.² Various synthetic methods have been proposed using chitosan and corresponding acyl agent (such as acid anhydride and acyl halide).³ In traditional heterogeneous methods, due to the low solubility of chitosan, toxic reagents or volatile organic solvents (such as acetone, dimethylformamide, and dimethylsulfoxide) and Brønsted acid (sulfuric acid or hydrofluoric acid) or base have been used as solvent and catalyst. Serious corrosion, pollution, and complicated separation problems have emerged consequently, and great efforts were made to purify the product and to deal with the waste. Employing acetic acid, sometimes, as well as formamide/methanol, formamide/ethanol, methanol, ethanol, and pyridine as solvents could carry out the

reaction in a homogeneous system. However, the above drawbacks cannot be overcome entirely; moreover, long reaction time, gel formed in reaction, and complex workup procedure would lead to new problems.⁴ Additionally, degradation of chitosan would occur in the process, which reduces the molecular weight of the product and restrict its application, especially for the fiber. At present, *N*-acyl chitosan fibers were usually prepared by a post-treatment of chitosan fibers with carboxylic anhydrides.^{5,6} However, not only this posttreatment technology is complicated, but some toxicant solvents must be used, the obtained acyl chitosan fibers were of poor mechanical properties. Therefore, seeking for a new green solvent to dissolve chitosan and carry out the acylation reaction in the homogeneous system to prepare *N*-acyl chitosan was important task to solve.

In the previous work, we used glycine chloride ([Gly]Cl)-aqueous solvent as dope to prepare the chitosan fibers by a wet-spinning process.⁷ Chitosan fibers, using 6.5% chitosan ($M_w = 1.5 \times 10^6$)/4% [Gly]Cl as spinning dope solution, showed good mechanical properties, despite other agents or posttreatments

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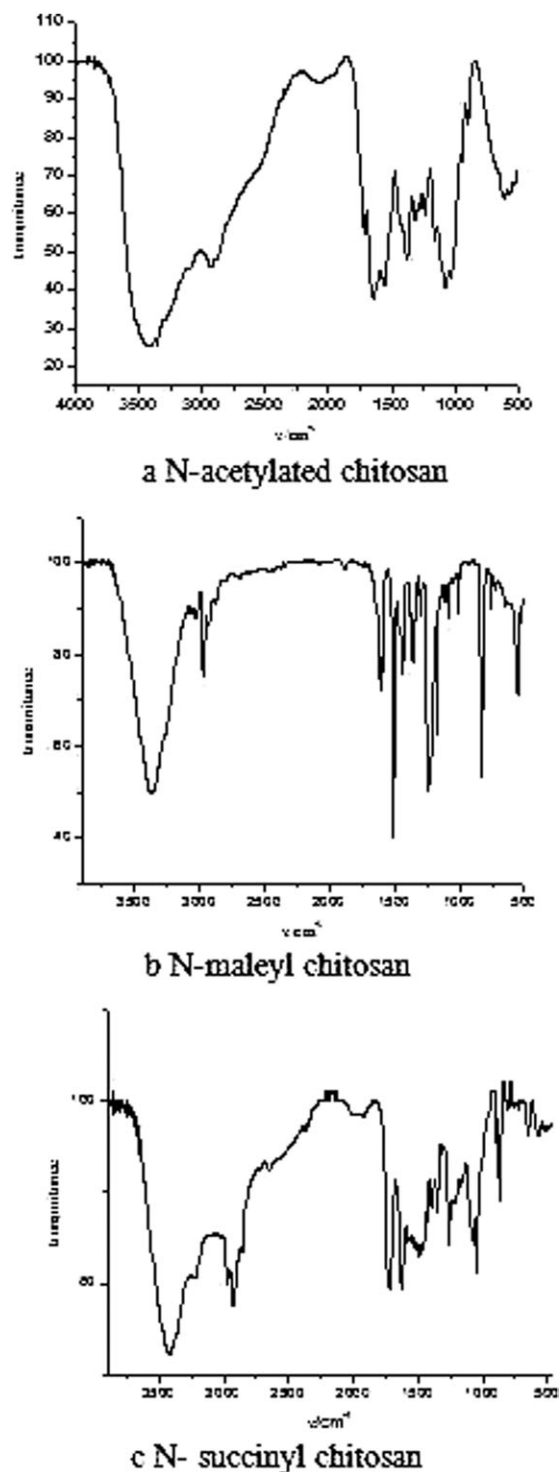


Figure 1. FT-IR spectrum of products.

compared with traditional methods used in the literature.⁸ The increase of breaking tenacity (from 0.86 to 3.77 cN/dex) and initial modulus (from 0.19 to 2.3) of the stretched fibers could be explained considering the evolution of the morphological properties. Moreover, due to the excellent stability of [Gly]Cl, the chitosan fiber by using the recycled [Gly]Cl as solution was of good property as well.

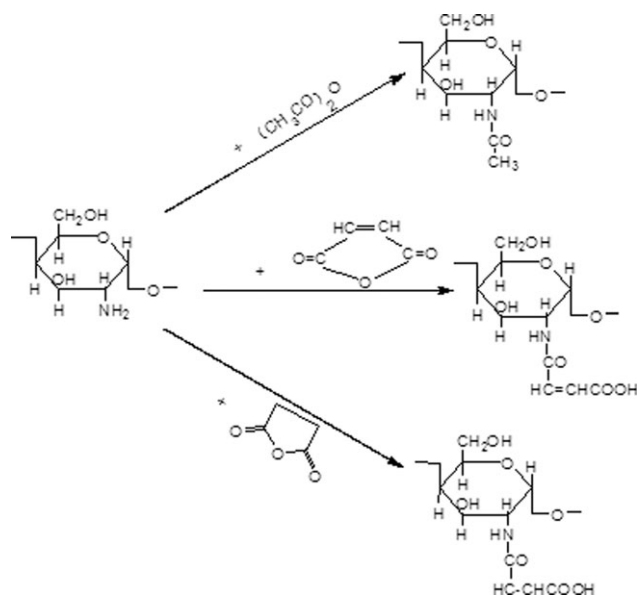


Figure 2. The formulas of *N*-acyl chitosan.

As part of our systematic research on dealing with chitosan in amino acid salt system, here we provided a benign approach to synthesize *N*-acyl chitosan, such as *N*-acetylated, *N*-maleyl, and *N*-succinyl chitosan. First, in order to achieve excellent performances of *N*-acyl chitosan on η , degree of substitution (DS), moisture absorbability, and retentivity, [Gly]Cl/chitosan/water homogenous systems, similar to ILs (ionic liquids) except for relatively high melt points, was tried. Next, the moisture absorbability and retentivity of the *N*-acyl chitosan prepared in this [Gly]Cl/water system were detected. Third, *N*-acyl chitosan fiber was synthesized using *N*-acyl chitosan as materials via [Gly]Cl-aqueous solvent as dope in a wet-spinning process, and the morphology and mechanical properties of the spun fibers were examined.

EXPERIMENTAL SECTION

Materials

Chitosan (the degree of deacetylation (DD) 86%, M_n 1.06×10^6), obtained from Yuhuan Chem. Co., Hangzhou city, China, was used only after drying without further purification. All other reagents were purchased from Aldrich.

Preparation and Characterization of [Gly]Cl

The amino acid salt was synthesized according to the method reported in the literature.⁹ [Gly]Cl: H₂O (0.55 mol) and HCl (0.08 mol, 36%) were added into a flask (100 mL) with stirrer, thermometer, condenser-Allihn type, and constant pressure spherical drop funnel. The mixture was stirred while Gly (0.05 mol) was slowly added in the flask. After Gly was dissolved completely in the mixture, the flask was heated to 60°C and the temperature was kept constant for 8 h. After completion of the reaction, the flask was cooled to room temperature and then a white solid was obtained after removing water from the product by vacuum. By washing with ethyl acetate, the resulting white precipitate [Gly]Cl was isolated by filtration and then dried *in vacuo* at 60°C for 24 h. Yield: 5.08 g (91%). The structure of

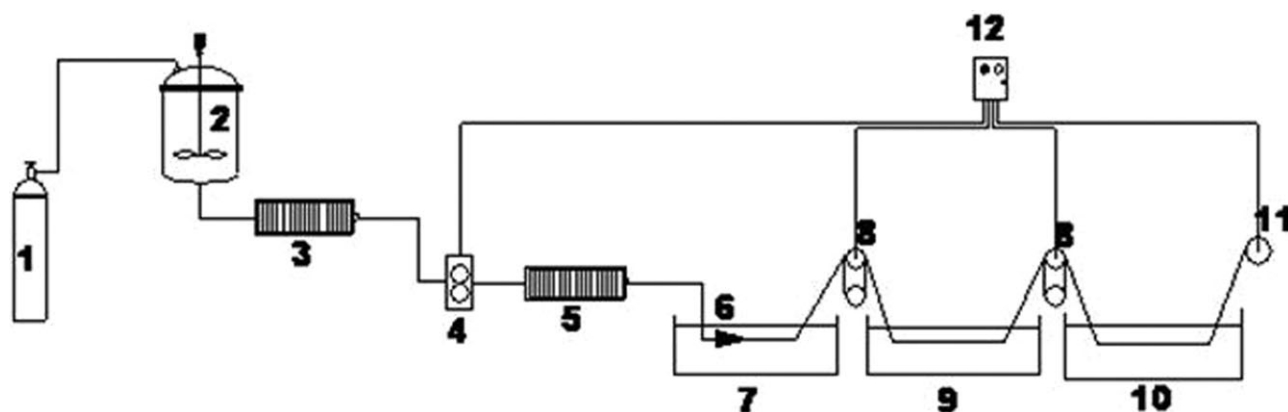


Figure 3. The Spinning unit. 1-nitrogen bottle; 2-dope reservoir; 3-filter; 4-metering pump; 5-filter; 6-spinning jet; 7-coagulation bath one; 8-advancing reels; 9-coagulation bath two; 10-washing bath; 11-idle rollers; 12-control cabinet.

the [Gly]Cl was verified by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FT-IR. [Gly]Cl: $^1\text{H-NMR}$ (500 MHz, D_2O): δ 3.78(s, 2H), 4.70 (s, 1H); $^{13}\text{C-NMR}$ (125 MHz, D_2O): δ 40.13, 170.08. The structure is as follows: $\text{Cl}^-[\text{NH}_3^+-\text{CH}_2-\text{COOH}]$ IR(KBr): ν 3434 (ν , $-\text{NH}_3^{*+}$ $-\text{CH}_2-\text{COOH}^*$), 3009 (ν_{as} , $-\text{CH}_2^*-\text{COOH}$), 1714 (ν_{as} , $-\text{C}=\text{O}^*$), 1596 (δ , $-\text{NH}_3^{*+}$), 1495 (δ , $-\text{CH}_2^*-\text{CO}-$), 1423 (δ , $-\text{COOH}^*$), 1255 (ν , $-\text{C}-\text{O}^*$), 1117 (ν , $-\text{N}-\text{C}^*$), 903 (ω , $-\text{O}-\text{H}^*$), 861 (δ , $-\text{N}-\text{H}^*$), 638, 496. The NMR spectra of the ionic liquids was recorded with a 500 MHz Bruker spectrometer in DMSO or CDCl_3 and calibrated with tetramethylsilane (TMS) as the internal reference. FT-IR was recorded with Nicolet-510P. The spectra were collected over the range of $4000\text{--}400\text{ cm}^{-1}$.

Reaction of *N*-Acyl Chitosan

One gram of chitosan was dissolved in 50 g of solvent (2% HAc aqueous solution and 2% [Gly]Cl salt aqueous solution, respectively) in a 100-mL round-bottom flask at room temperature for 10 min with agitation, to form homogeneous system. The acylating agent (acetic anhydride, succinic anhydride, and maleic anhydride) was added into the homogeneous system under agitation, $n(\text{acylating agent}):n(\text{chitosan}) = 2.75$, reaction temperature was 60°C , reaction time was 5 h. After completion of the reaction, acetone was added in the homogeneous system. The product was deposited and dried at 40°C under vacuum, then was characterized by FT-IR (Figure 1). After the reactant solvent was collected and distilled, the [Gly]Cl salt could be recovered and reused. The formulas are shown in Figure 2.

Determination of Degree of Substitution

The DS value of each samples were estimated by the method of potentiometric titration.^{10,11} The alkalimetric curves were recorded on a DELTA-320-S pH meter. *N*-acyl Chitosan (ca. 100

mg) is dissolved in a known volume of aqueous HCl (0.010 mol L^{-1}) and the solution is then titrated with 0.1 mol L^{-1} NaOH, while the pH of the solution is measured at constant ionic strength (0.1 mol L^{-1} NaCl). The graph with the variation of pH versus the added volume of base has two inflexion points: the first corresponds to neutralization of HCl and the second to neutralization of the ammonium ions from chitosan. The difference between the two inflexion points gives the amount of amino groups in *N*-acyl chitosan (A). The DS is obtained from formula: $\%DS = 100 - \%A$.

Determination of η of Chitosan and *N*-Acyl Chitosan

The viscosities of chitosan and *N*-acyl chitosan samples were measured in a solution of 0.20 mol/L NaCl + 0.1 mol/L CH_3COOH at 25°C using an ubbelohde capillary viscometer ($\phi = 0.5\text{--}0.6\text{ mm}$).¹²

Determination of Crystallinity

X-ray powder diffraction patterns of the samples were obtained on a XB-3A instrument using monochromatic Cu K α radiation ($\lambda = 0.15418\text{ nm}$). It was operated at 40 kV and 100 mA. The experimental conditions correspond to a step width of 0.02° and scan speed of $20/\text{min}$ and diffraction region $2\theta = 10\text{--}45^\circ$.

Determination of the Moisture-Absorption and -Retention Performance of Samples

Samples were put into a dryer with phosphorus pentachloride for 12 h under vacuum at room temperature. (1) The moisture-absorption performance determination: 3 cmd weighing bottles filled with the accurately weighing samples (m_0 , around 0.5 g of each) were placed into the saturated sulfate ammonium solution (relative humidity = 81%) for 10, 20, 30, 40, and 50 h. The weight of experimental sample (m_n) and former sample (m_0)

Table I. Synthesis of *N*-Acyl Chitosan in Different System

Solvent	<i>N</i> -acetylated		<i>N</i> -maleyl		<i>N</i> -succinyl	
	Inherent viscosity (mL/g)	DS (%)	Inherent viscosity (mL/g)	DS (%)	Inherent viscosity (mL/g)	DS (%)
Acetic acid	525.95	74.0	529.22	73.3	493.22	62.5
[Gly]Cl	627.14	83.2	583.19	80.5	585.79	81.6

Table II. The Reusability Performance of [Gly]Cl

Cycle	Samples	Inherent viscosity (mL/g)	DS (%)
1	N-acetylated	627.14	83.2
	N-maleyl	583.19	80.5
	N-succinyl	585.79	81.6
2	N-acetylated	625.85	83.3
	N-maleyl	583.84	80.4
	N-succinyl	582.55	81.2
3	N-acetylated	624.56	83.7
	N-maleyl	582.55	81.1
	N-succinyl	581.90	81.5
4	N-acetylated	625.20	83.5
	N-maleyl	581.90	80.6
	N-succinyl	583.19	81.1
5	N-acetylated	623.91	83.7
	N-maleyl	581.25	80.5
	N-succinyl	582.55	81.4

was compared. Moisture-absorption ratio (%) = $100 (m_n - m_0)/m_0$; (2) The moisture-retention performance determination: 3 cmd weighing bottles filled with the accurate weighing samples (around 0.5 g of each) were added with 10 wt % water (gross weight = H_0 of each) and placed into the dry silica gel for 10, 20, 30, 40, and 50 h. Compared the weight of experimental sample (H_n) with former sample (H_0). Residual ratio of water (%) = $100H_n/H_0$ %.

Wet Spinning of Acetylated Chitosan Fiber

A typical spinning dope solution was prepared by dissolving acetylated chitosan in 400 mL of 4% [Gly]Cl (w/w) aqueous solution at 30°C according to our previous work.⁷ The spinning dope solution was filtered through a candle filter system before adding it to the reservoir of the spinning system, where it was degassed under vacuum. A laboratory scale extrusion unit was used, composed of a reservoir, a metering pump (1 mL rev⁻¹), and a spinneret (20 holes, 80 μm diameter). The filaments were coagulated in a dilute Na₂SO₄/C₂H₅OH bath, with an immersion length of ca. 100 cm. The take-up rollers, drawing system, drying rollers, and the winding up procedure were described previously. The filaments were washed and dried by freeze-drying (Figure 3).

Characterization of N-Acetylated Chitosan Fiber

Mechanical properties of the acetylated chitosan yarn samples, such as breaking strength, breaking tenacity, elongation at break, and initial modulus, were measured on an Instron tensile tester, model 1122, with load cell-type 1105. The gauge length was 20 mm and the extension rate was 20 mm min⁻¹. The test was performed at 20°C, 65% RH. The figures quoted are the averages of 10 tests; the standard deviation was generally less than 5%. When required, tests were also performed on yarns, previously immersed in water at room temperature, to obtain wet strength values.

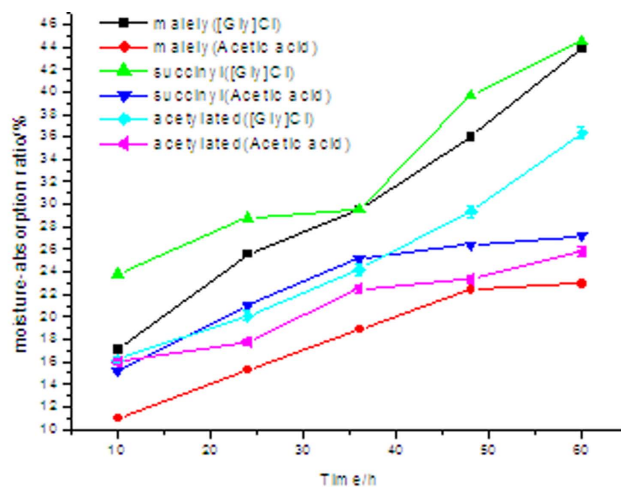
Morphological structures of the fiber were observed by a HITACHI S-2600HS scanning electron microscope (SEM) with a 15 kV accelerated voltage. Samples were gold coated by ion sputter-

ing with a JEOL JFC-1100-E and current 10 mA for 90 s before observation.

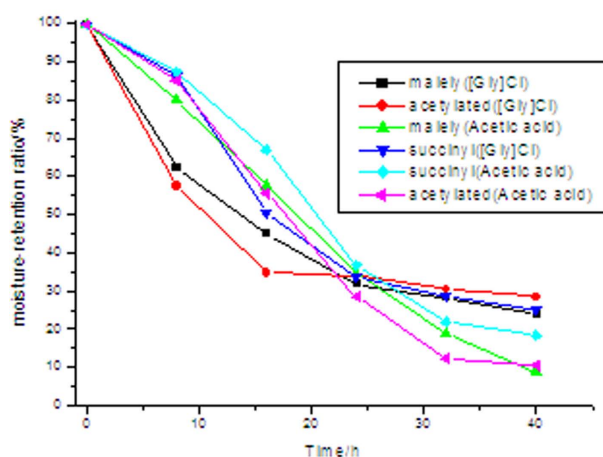
The average diameter of fibers was evaluated using a transmission optical microscope (Leitz), from 10 values measured on different points of the monofilament.

The denier ($D = \text{weight (g)}/9000 \text{ m}$ of monofilament) of each chitosan fiber sample was determined by weighing at least 20 m of chitosan monofilament. The length (L) of the monofilament was determined by two methods. The first method measured the length of several fibers to achieve a sufficient total length over 20 m. The results of the pilot method controlled the second one. Thus, the length was the result of the multiplication of a time of spinning (min) by the roller 2 speed (v_2 in m/min). In both cases, the precision was of 10⁻³ g. An average denier was calculated from the two methods.

After measuring the diameter and the denier of each sample of fiber, we could deduce their density by the following equation¹³:



a: moisture-absorption (RH=81%)



b: moisture-retention (silica gel)

Figure 4. (a) The moisture-absorption (RH = 81%) and (b) moisture-retention (silica gel) capacity of N-acyl chitosan from different systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

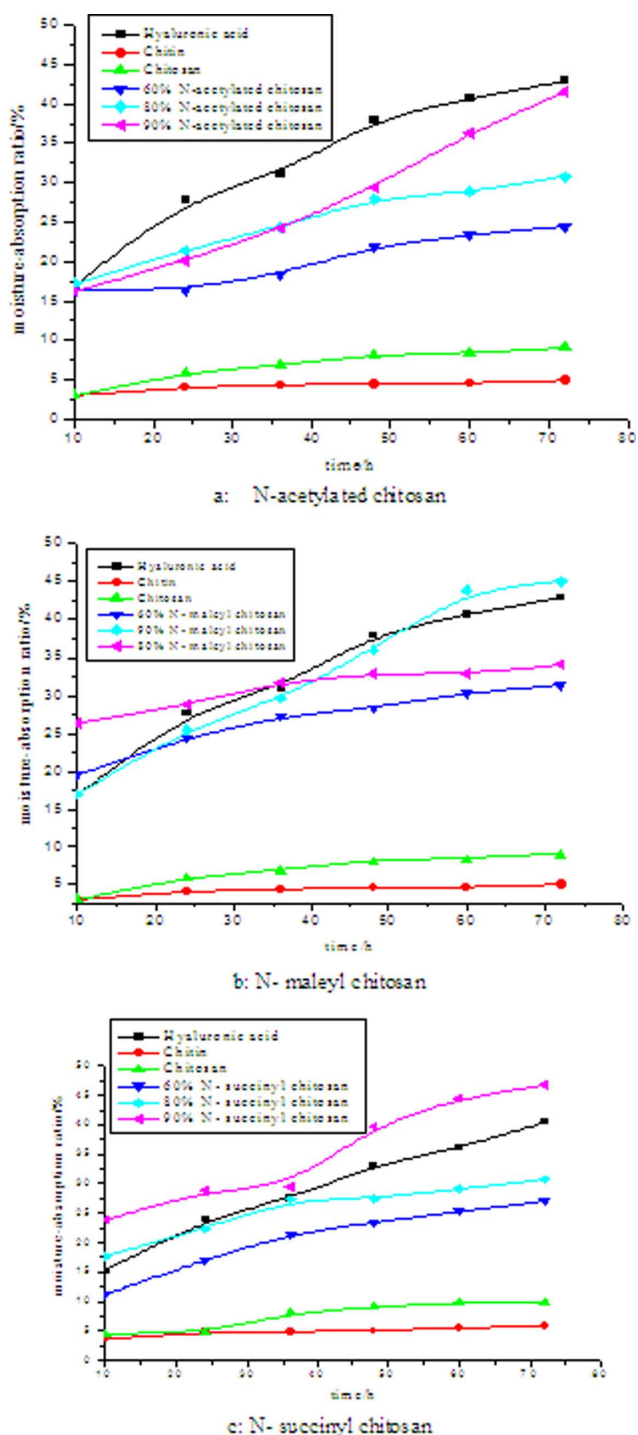


Figure 5. Moisture-absorption capacity of chitin, chitosan, *N*-acyl chitosan, and hyaluronic acid (RH = 81%): (a) *N*-acetylated chitosan, (b) *N*-maleyl chitosan, and (c) *N*-succinyl chitosan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$d = 20\sqrt{\frac{T}{\pi\rho}} \quad \text{or} \quad d = 20\sqrt{\frac{10D/9}{\pi\rho}}$$

where d is the diameter (μm), T is the weight of 10,000 m of monofilament (dtex), q is the density (g cm^{-3}), and D is the denier.

RESULTS AND DISCUSSION

N-Acyl Chitosan

Three kinds of *N*-acyl chitosan (acetylated, maleyl, and succinyl) were prepared in [Gly]Cl and acetic acid aqueous system, respectively, and the results are shown in Table I. From the Table I, it could be seen that *N*-acyl chitosan was of higher DS and η in [Gly]Cl aqueous system than that in traditional acetic acid aqueous system. The [Gly]Cl aqueous system was of better solubility for chitosan than acetic acid.^{14–16} When chitosan was dissolved in the system of [Gly]Cl/water, a strong hydrogen bonding ($\text{O}=\text{C}-\text{O}\cdots\text{NH}$) could disrupt between molecular chains due to ion effect of $[\text{Gly}]^+$ and Cl^- groups.^{17–19} Therefore, the N-2, as a proton donor, was exposed to $\text{O}=\text{C}-^*\text{O}-$ of an adjacent molecular to prepare *N*-acyl chitosan easily.⁷

The Reusability of [Gly]Cl/Water System

From Table II, the DS and η of *N*-acyl chitosan showed slight change with the increasing of repeated use times of [Gly]Cl, which suggested that [Gly]Cl is of excellent stability and can be recycled. The slight fluctuation on property of *N*-acyl chitosan was caused by the inevitable loss of [Gly]Cl during the regeneration process.

Moisture-Absorption and -Retention Properties of *N*-Acyl Chitosan

The moisture-absorption and -retention curves of three kinds of different *N*-acyl chitosan from different system are shown in Figure 4. From Figure 4, it could be seen that the moisture-absorption (a) and moisture-retention (b) properties of *N*-acyl chitosan from [Gly]Cl aqueous system were better than those from acetic acid aqueous system. This strongly suggested that the driving force for aggregates, i.e., the intermolecular hydrogen bonds of molecular chains, which affected the interaction between water and polymer chains directly, may be a very important factor to regulate moisture-absorption and -retention ability of *N*-acyl chitosan. Under high relative humidity conditions (RH 81%), water molecules were accessible to get the surface of the sugar residues and readily to develop hydrogen-bond interactions with the *N*-acyl chitosan molecular chains. As a result, they interwoven between chains or chain sheets in the network.²⁰ From the

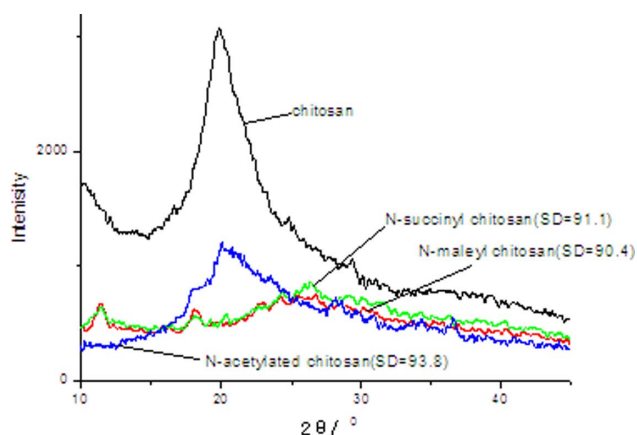


Figure 6. XRD of chitosan and *N*-acyl chitosan obtained from [Gly]Cl/water system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Influence of Different Stretching Ratio on Mechanical Properties of Chitosan Fiber

Stretching ratio	Breaking Tenacity /cN/dtex	Elongation at break/%	Flexural strength/cN/dtex	Initial modulus/ cN/dtex	Denier/dT
1.2	0.743	13.736	1.112	0.133	7.1
1.3	1.148	10.112	0.917	0.712	9.515
1.35	2.072	5.144	1.033	1.348	5.93
1.45	2.295	10.186	1.0	1.356	5.423

Dope: 6.5% *N*-acyl chitosan in 4% [Gly]Cl, extrusion rate: 13.6 m/min⁻¹, Yarn dried with freeze drying $T = 20^{\circ}\text{C} \pm 2^{\circ}\text{C}$, water content = (35 ± 5)% (w/w).

moisture-absorption properties of the *N*-acyl chitosan prepared from [Gly]Cl aqueous system (Figure 5), all *N*-acyl chitosans showed better moisture-absorption properties than chitosan and chitin, indicating introduction of the acyl group was a convenient and effective method to improve moisture-absorption ability of chitosan. With the increasing of DS, moisture-absorption ability

of *N*-acyl chitosan increased accordingly. Especially, *N*-maleyl and *N*-succinyl chitosan were of better moisture-absorption ability than *N*-acetylated chitosan. This could be explained from the crystallinity of samples (Figure 6), it could be seen that *N*-acetylated chitosan showed a slight, broad diffraction peak centered near $2\theta = 20^{\circ}$ and *N*-maleyl and *N*-succinyl chitosan showed a

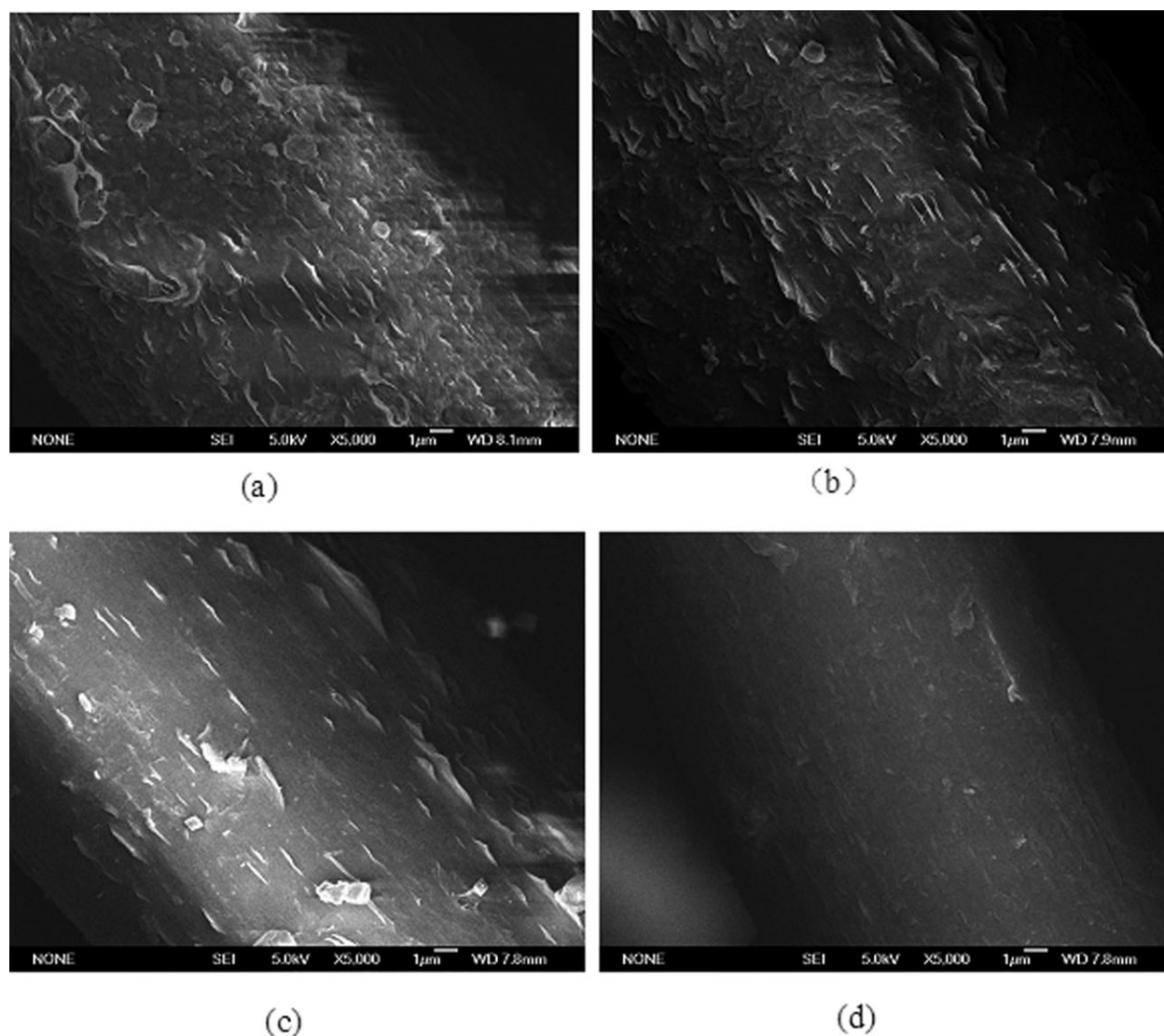


Figure 7. SEM of *N*-acetylated chitosan fiber of different stretching ratio by wet spinning: (a) stretching 1.2 times, (b) stretching 1.3 times, (c) stretching 1.35 times, and (d) stretching 1.45 times.

slight, broad diffraction peak centered near $2\theta = 26^\circ$, and no diffraction peak centered near $2\theta = 20^\circ$ compared with crystal chitosan. This result implied that the crystalline domains in the chitosan particles were incompletely disrupted by malely and succinyl reaction. Anyway, we can conceive that such a reaction should make *N*-malely and *N*-succinyl chitosan more flexible than that of crystal chitosan and *N*-acetylated chitosan.²¹ Therefore, it also suggested that the moisture-absorption capacity of *N*-acyl chitosan not only was related with the DS but also with the steric hindrance of acyl group.²² High DS means that abundant acyl agent molecules entered into the skeleton of chitosan and led the crystallinity of chitosan to decrease (Figure 6). Moreover, the increase of the hydrophilic acyl group with DS would also make the improvement in moisture-absorption capacity. For the same reason, when the DS was the same, the bigger the steric hindrance of acyl group was, the stronger the ability to destroy the crystallinity. In addition, acyl group could induce the increase of the stiffness and length of chitosan chain, as well as the electrostatic repulsion of carboxyl negatively charged matter would enhance the surface area.²³ As a result of the synergy between intermolecular hydrogen bond and electric charge, the chain of chitosan became a network which would make tight coupling of water molecular and chitosan chain, accordingly, the moisture-absorption capacity was increased.²⁰ When DS of *N*-malely and *N*-succinyl chitosan was more than 80%, all samples showed better moisture-absorption capacity than HA and had potential to use as moisture-retention ingredient, e.g., in cosmetics.²⁴

Fiber of Acetylated Chitosan

The parameter of viscosity was regarded as the primary criteria for the selection of suitable kind and concentration of *N*-acyl chitosan/4% [Gly]Cl spinning solution. From Table I, it could be seen that *N*-acetylated chitosan was of highest inherent viscosity among the three acyl chitosan and was of best crystallinity (Figure 6). For fiber obtained with strong mechanical properties, *N*-acetylated chitosan was selected as materials. According to our previous research,⁷ a 7% *N*-acetylated chitosan solution was used as the spinning dope, the mixture of $v(2\%Na_2SO_4) : v(C_2H_5OH) = 10 : 3$ was selected as coagulator and the process of coagulation was carried out at 20–25°C.

When dope ejected from spinneret orifice, fiber received force of extrusion and friction from ambient spinneret orifice, and the force made macromolecular association of fiber orderly to arrange along the axial of orifice.²⁵ However, the orientation of fiber was instability, and swell effect could be produced during the process of fiber extrusion, meanwhile the effect led to macromolecule newly disordered astatic state after being ejected. Therefore, the only way to enhance the strength of fiber was drawing. In this part, the mechanical property and morphology of *N*-acetylated chitosan fibers were investigated after drawn in 1.2, 1.3, 1.35, 1.45 times (Table III). From the data of Table III, with the increasing of drawing times, the mechanical property obviously strengthened and tenacity strength hugely enhanced. When the drawing times were 1.45, the mechanical property of *N*-acetylated chitosan reached 2.295 cN/dT, which was beyond the mechanical property of *N*-acetylated chitosan using a posttreatment method in the present report.^{5,6} When the drawing times was further increased, fiber would be cracked. In addition, the toughness and

strength of fibers were improved; it agreed with that chitosan fiber was prepared using [Gly]Cl as dope.⁷ It can also be seen from the SEM (Figure 7); the fiber was smoother and denser with the increasing of times of drawing. It was suggested that with the increasing of drawing times, macromolecular fibers were more uniformly arranged along the direction of force.²⁶

CONCLUSIONS

N-acyl (*N*-acetyl, *N*-malely, and *N*-succinyl) chitosan could be synthesized in the homogeneous [Gly]Cl aqueous solution system, which possessed excellent solubility for chitosan. *N*-acyl chitosan prepared in this [Gly]Cl aqueous solution system showed the better moisture-absorption and -retention performance and higher η and DS than that prepared in traditional solvents. In addition, the moisture-absorption capacity was not only related with the DS but also with the steric hindrance of acyl group. The DS was higher, and the steric hindrance of acyl group was bigger, consequently the moisture-absorption capacity was better. The separation and recycling of [Gly]Cl were easy and only a slight activity lost. At the same time, *N*-acetylated chitosan fiber with good mechanical properties was prepared by using 7% *N*-acetylated chitosan/4%[Gly]Cl as spinning dope solution, without any agents or posttreatments commonly used in the literature. Thus, the improved mechanical properties of the wet-spun *N*-acetylated chitosan fibers prepared in this study should contribute to their use in biomedical applications, such as hernioplasty, suturation, or wrinkle filling.

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