

Solubility and property of chitin in NaOH/urea aqueous solution

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Abstract

NaOH/urea aqueous solution has been used as a solvent for chitin for the first time. Effects of this solvent composition and temperature on the solubility and stability of chitin solution were studied with an optical microscope, from which 8 wt% NaOH/4 wt% urea concentrations were deduced as suitable and -20°C as the appropriate temperature. The original and regenerated chitin were characterized by viscosity, elemental analysis, FI-IR and X-RD analysis, and the effect of solvent composition and temperature on chitin structure was investigated. It was inferred that 8 wt% NaOH/4 wt% urea solvent under low temperature adventitiously has little effect on chitin structure and the urea is of benefit to the stability of chitin solution. In addition, the rheological properties suggested that chitin aqueous solution in high concentration is a pseudoplastic fluid and that chitin aqueous solution in low concentrations is a Newtonian fluid. This chitin aqueous solution is sensitive to temperature and will transform it to a gel when temperature increases.

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1. Introduction

Chitin, a linear polysaccharide composed of (1–4)-linked 2-acetamido-2-deoxy- β -D-glucopyranose units, is the second most abundant form of polymerized carbon found in nature. Every year, approximately 10 billion tons of chitin are produced by crustaceans, molluscs, insects, fungi some algae and related organisms, etc (Rege & Block, 1999; Tolaimate et al., 2000). Chitin is biorenewable, biocompatible, environmentally friendly, biodegradable and biofunctional, and has proved useful as chelating agents, drug carriers, membranes, water treatment additives, biodegradable pressure-sensitive adhesive tape, and wound-healing agents and for a number of other important applications (Chen, Du, Wu, & Xiao, 2002; Xu, McCarthy, Gross, &

Kaplan, 1996), with a result that more and more attention is paid to this characteristic biomaterial.

However chitin is not widely used by the pharmaceutical industry at present. Its limited utility, principally, is the result of its poor solubility characteristics. Chitin is insoluble in dilute aqueous solvents and common organic solvents, because of its strong intra- and inter-hydrogen bonds. However, its derivative, chitosan, prepared by deacetylation and depolymerization of native chitin, is soluble in dilute acids. Hence, chitosan has been widely studied and applied. On the other hand, serious pollutions have occurred in the process of producing chitosan from chitin with plenty of alkali.

The molecular weight and structure of chitosan are different to chitin after the deacetylation and depolymerization, which is unfavorable for some applications, such as forming fibers. Various attempts have been made to improve the solubility of chitin while retaining its molecular structure. The main solvents used have been

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chlorohydrin/inorganic acid; LiCl/DMF; LiCl/DMAc; LiCl/NMP; concentrated mineral acids (such as HCl, H₂SO₄); 40 wt% NaOH (Austin, 1978), which fall short of toxicity, pollution, depolymerization and high cost.

Chitin can be dissolved when an alkaline suspension of the polymer is mixed with ice (Sannan, Kurita, & Iwakura, 1975). Plenty of researches have revealed that frozen alkali chitin has already been chosen as a convenient precursor for efficient modifications (Dong, Wu, & Wang, 2001; Hirano, 1988; Tokura & Tamura, 2001; Tokura, Nishi, Tsutsumi, & Somorin, 1983). An interesting study by Feng et al. concerning the influence of alkali-freezing treatment on the solid state structure of chitin, for the sake of soaking chitin in frozen sodium hydroxide for further modification, suggested that alkali-freezing treatment of chitin for several days is suitable and sufficient (Feng, Liu, & Hu, 2004). Powdered chitin suspended in 40% (w/w) NaOH and kept at 4 °C for 72 h. and then dilution to 10% (w/w) NaOH using crushed ice resulted in a viscous solution of 2.25 mg/mL chitin (Einbu, Naess, Elgsaeter, & Vårum, 2004). Dilute solution properties of chitin of various molecular weights in alkali have been determined, showing that alkali is a good solvent to chitin. This solvent system offers attractive alternative solvents to chitin (Einbu et al., 2004).

Chitin is structurally similar to cellulose which is still extensively used in the viscose rayon industry. Both of them have analogical properties including the same solvents such as *N,N*-dimethylacetamide–LiCl. Recently, a novel cellulose solvent composition of urea and NaOH was studied (Zhou & Zhang, 2000), and it was discovered that the solubility of cellulose in 6–8 wt% NaOH aqueous solutions was significantly improved by addition of 2–4 wt% urea. Also the degradation rate of cellulose in 6 wt% NaOH/4 wt% urea aqueous solution was obviously slower than in cuoxam solution (Zhou & Zhang, 2000), from which novel regenerated cellulose fibers have been successfully spun (Cai et al., 2004).

Novel solvents of chitin are currently the quest and key to its further research and application, which makes for its further modification and the possibility of new forms of chitin fibre through spinning such solutions. Given the foregoing discovery for cellulose, in the current work, NaOH/urea aqueous solution has been used as a solvent of chitin for the first time.

2. Materials and methods

2.1. Materials

Chitin was purchased from Dalian Xindie Chitin Co.Ltd, powered, and sifted to select less than 0.635 mm diameter particles. The viscosity-average molecular weight was 1.88×10^6 (Ubbelohde viscometer, Poirier & Charlet, 2002). The degree of acetylation (DA) was measured to be 0.98 using elemental analysis (Xu et al., 1996). Other agents were of analytical grade.

2.2. Dissolution of chitin

The NaOH/urea aqueous solutions were prepared by changing the concentration of NaOH such as 0, 2, 4, 6, 8, 10 and 12 wt% in lots turn, as well as changing the concentration of urea such as 0, 2, 4, 6, and 8 wt%. Chitin powder (4 g lots) was dispersed in NaOH/urea aqueous solutions (200 g each). The suspensions were kept at –20 °C and stirred twice over 36 h. The swollen or dissolved state was observed through an optical microscope (Nikon Eclipse E600, 40×10 times) at environmental temperature.

Chitin powder (4 g) was dispersed in 8 wt% NaOH/4 wt% urea aqueous solvent (200 g, solvent coded as solvent S8-4). The suspensions were maintained at different temperatures (10, 0, –10, –15, –20, –30, –40 and –80 °C), and stirred for 36 h. Again the swollen or dissolved state was observed optically.

2.3. Solubility of chitin

The chitin solutions prepared hereinbefore were centrifuged at 3500g for 20 min at 10 °C. To determine the amounts of dissolved chitin, the insoluble chitin was washed with NaOH/urea aqueous solutions firstly and subsequently with water, then evaporated in vacuum and quantified. The solubility was calculated from the following formula.

$$S_a = [(4 - W_1)/4] \times 100\%$$

where W_1 denotes the weight (g) of the insoluble chitin. All the experiments were done in triplicate.

2.4. Measurement of viscosity

Chitin powder was dispersed in solvent S8-4 (see above). The suspensions were kept at –20 °C, and stirred for 36 h. The chitin solutions were centrifuged at 3500g at 10 °C for 20 min. and 2.0 wt% chitin solution was prepared (coded as S8-4-CH2). The chitin was regenerated by being precipitated by the addition of 10 wt% H₂SO₄ – the volume of 10 wt% H₂SO₄ was equal to that of chitin solution, in order to precipitate chitin fully. Then the precipitate was washed with distilled water, and after drying at 30 °C in vacuo; the product was coded as CH1.

The S8-4-CH2 solution was stored at –20 °C and the chitin was precipitated after 5, 10, 20 days – products were coded as CH2, CH3, CH4, respectively. The intrinsic viscosities of CH0, CH1, CH2, CH3, CH4 were determined after dissolving the chitin at 0.03 g/dL in 5 wt% LiCl in DMAc. The molecular weight of CH0, CH1, CH2, CH3, CH4 were calculated from the Mark–Houwink–Sakurada equation (Poirier & Charlet, 2002):

$$[\eta] = 7.6 \times 10^{-5} M_w^{0.95}.$$

The viscometer has a negligible kinetic energy correction for solvent flow time over (150 s) and so the kinetic energy

correction was always negligible. All calculations were based on chitin solutions of relative viscosity $\eta_{\text{rel}} \leq 2$. To obtain more accurate values, the intrinsic viscosities were determined as the average of extrapolating both η_{sp}/c and $\log \eta_{\text{rel}}/c$ to 0 concentration (Stokke, Elgsaeter, Bjørnstad, & Lund, 1992).

2.5. Measurement of the degree of acetylation

The C, H, N contents of chitin were determined by elemental analysis on VarioEL III equipment, Vario, Hanau, (Germany). Values change according to the degree of acetylation of chitin. The structural formula of chitosan monomer full deacetylated is $\text{C}_6\text{NO}_4\text{H}_{11}$, whereas the structural formula of full acetylated chitin monomer is $\text{C}_8\text{NO}_6\text{H}_{13}$. The degree of acetylation of CH0, CH1, CH2, CH3, CH4 determined by elemental analysis was calculated using the following equation (Xu et al., 1996):

$$\text{DA} = [(C/N - 5.14)/1.72] \times 100\%$$

where C/N is the ratio (w/w) of carbon to nitrogen.

2.6. Characterization of chitin by FT-IR

The FT-IR spectra of CH0, CH1, CH2 were recorded on an FT-IR spectrometer (Nicolet, Model Impact 410, WI) at ambient temperature.

2.7. X-RD profiles of chitin

The X-ray diffraction (XRD) profiles of the sample CH0, CH1, CH2 were measured with a Shimadzu Lab-XRD-6000X diffractometer (Shimadzu, Kyoto, Japan) under 20 °C, using a $\text{CuK}\alpha$ target at 40 kV and 50 mA, DS/SS 0.5°. The scanning rate was 4°/min and the diffraction angle (2θ) ranged from 5° to 45°.

2.8. Rheological measurement

The S8-4-CH2 chitin solution was diluted with the S8-4 solvent to prepare 1.5, 1.0, 0.5 wt% chitin solutions, which were coded as S8-4-CH1.5, S8-4-CH1, S8-4-CH0.5, respectively. The steady shear viscosities of these were determined rheometrically at 20 °C, angular frequency 1 rad s^{-1} , Rate 0–100 s^{-1} . The gelation temperature of the S8-4-CH2, S8-4-CH1.5, S8-4-CH1, S8-4-CH0.5 solutions were determined rheometrically: angular frequency 1 rad s^{-1} , temperature range 5–50 °C.

The chitin solutions with concentration range 0.5–2 wt% were characterized rheologically using the steady shear and dynamic oscillator tests. All rheological measurements were performed on a Rheometric Scientific ARES controlled strain rheometer (TA Instruments, New Castle, USA). The rheometer was equipped with two sensitive force transducers for torque measurements ranging from 0.004 to 100 g cm. A Couette (two concentric cylinders) cell geometry was used for monitoring the steady-state shear

flow and dynamic rheology of the samples moduli. The degassed solution of 10 mL was heated or cooled to the desired temperature within ± 0.5 °C directly in the rheometer (without shearing or oscillating) and then covered with mineral oil in order to prevent evaporation during the measurements.

For the temperature sweep measurements to determine the gelation temperature, oscillatory measurements were performed at 1 Hz, while the temperature was increased at 1 °C/min between 5 and 50 °C. The dynamic viscoelastic functions such as the dynamic shear storage modulus (G') and loss modulus (G'') were measured as a function of temperature. The values of the strain amplitude were checked to ensure that all measurements were carried out within the linear viscoelastic regime, where the G' and G'' are independent of the strain amplitude according to the result of dynamic strain sweep. Plots were made of the log apparent viscosity vs. log shear rate (from 0.1 to 100 1/s) to determine zero-shear viscosities. It showed that all the solutions exhibited linear viscoelastic behavior at 1 Hz with a constant shear strain of 100–400%.

3. Results and discussion

3.1. Dissolution conditions of chitin in NaOH/urea aqueous solution

3.1.1. NaOH/urea aqueous solvent effect

The dissolution state of chitin in NaOH/urea aqueous solution could be observed through naked eye and optical microscope. Chitin was an opaque solid before being dissolved, and was translucent when swollen, and was transparent in solution after being dissolved. The NaOH concentration in NaOH/urea aqueous solution had great effects on the solubility of chitin, as shown in Table 1. Chitin could not be dissolved when the concentration of NaOH was lower than 4 wt%, but it was soluble in 6–8 wt% NaOH. The solubility of chitin in 6–10 wt% NaOH aqueous solution was significantly improved by 2–8 wt% urea, and the stability of chitin solution in 6–10 wt% NaOH aqueous solution was enhanced obviously by 2–8 wt% urea, whereas the stability of chitin solution decreased when the concentration of NaOH was more than 12 wt%. It can be inferred that NaOH breaks the inter- and intra-hydrogen bonds while urea prevented the aggregation of chitin molecules and kept the stability of chitin aqueous solution (Zhou & Zhang, 2000). So the solubility of chitin increases following the increasing NaOH concentration and the stability of chitin solution was enhanced while the urea concentration increased from 2 wt% to 8 wt%. Aqueous 8 wt% NaOH/4 wt% urea solution was regarded as the appropriate solvent for chitin. The aqueous chitin solution in NaOH/urea was homogeneous and transparent.

3.1.2. Temperature treatment effects

The solubility and stability of chitin in 8 wt% NaOH/4 wt% urea aqueous solution are decidedly a function of

Table 1
Assessment of the dissolution of chitin in NaOH/urea aqueous solution at $-20\text{ }^{\circ}\text{C}$

Urea concentration (wt%)	NaOH concentration (wt%)					
	2	4	6	8	10	12
0.0						
Dissolution state	Undissolved	Undissolved	Swollen	Unstable	Unstable	Unstable
Solubility $S_a(\%)$	0	0	20	50	80	85
2.0						
Dissolution state	Undissolved	Undissolved	Swollen	Unstable	Unstable	Unstable
Solubility $S_a(\%)$	0	0	20	60	85	88
4.0						
Dissolution state	Undissolved	Undissolved	Unstable	Good	Good	Unstable
Solubility $S_a(\%)$	0	0	30	85	90	90
6.0						
Dissolution state	Undissolved	Undissolved	Good	Good	Good	Unstable
Solubility $S_a(\%)$	0	0	30	86	90	91
8.0						
Dissolution state	Undissolved	Undissolved	Good	Good	Good	Unstable
Solubility $S_a(\%)$	0	0	30	88	91	91

temperature. Chitin could not be dissolved in 8 wt% NaOH/4 wt% urea aqueous solution when the treatment temperature is higher than $-20\text{ }^{\circ}\text{C}$. At the temperature of $-20\text{ }^{\circ}\text{C}$, chitin has greater solubility and better stability than at other temperatures (Table 2). It is suggested that the appropriate treatment temperature is related to the freezing point of chitin in 8 wt% NaOH/4 wt% urea aqueous solution, which is $-19\text{ }^{\circ}\text{C}$ as measured practically. The solubility decreases with decreasing in temperature when temperature is lower than $-30\text{ }^{\circ}\text{C}$. When treatment temperature is higher than the freezing point, water molecules did not freeze and expand, and chitin could not be dissolved. When the treatment temperature decreases to the freezing point, chitin could be dissolved.

The process of chitin being dissolved is shown in Fig. 1. Chitin is soaked in 8 wt% NaOH/4 wt% urea aqueous solution at ambient temperature (a), and water molecules enter the chitin molecular chain assisted by the NaOH (b), and then freeze and expand at the freezing point when water and sodium hydroxide molecule separate out together, and break the inter- and intra-hydrogen bonds (c), promoting the solubility of chitin (d). However, when the treatment temperature is lower than $-30\text{ }^{\circ}\text{C}$, the freezing and expansion process is shorter and the expanding effect becomes weaker compared with that at (or lower than the freezing point nearly, such as $-20\text{ }^{\circ}\text{C}$) the freezing point, which reduces its solubility.

3.2. Effect of the solvent on the structure of chitin

3.2.1. Effect of the solvent on the molecular weight of chitin

Molecular weight is an important structural parameter of chitin, which can be calculated from the Mark–Houwink–Sakurada equation. The viscosity measurements were performed using an Ubbelohde capillary viscometer. In chitin aqueous solution S8-4-CH₂, the molecular weight of chitin decreased rapidly in the beginning of the dissolution process, and then reduced more slowly. The molecular weight of the chitin decreased from 1.88×10^6 to 1.68×10^6 in the process of dissolution (10.6%), and the molecular weight of chitin reduced by 9.5% from 1.68×10^6 to 1.52×10^6 during the subsequent 20 days storage (Fig. 2). This degradation of chitin in alkali was reported by Einbu et al. (2004). This indicates that the effect of the NaOH/urea solvent on the molecular weight of chitin is little, which is lesser than the effect of NaOH solution reported elsewhere (Noishiki et al., 2003; Einbu et al., 2004).

3.2.2. Effect of the solvent on the degree of acetylation of chitin

The degree of acetylation (DA) is also an important structural parameter of chitin. Alkali processing usually causes deacetylation. Cho et al. prepared partially deacetylated chitins with different degrees of deacetylation (DD) by alkaline treatment under homogeneous conditions,

Table 2
The degree of dissolution of chitin in 8 wt% NaOH/4 wt% urea aqueous solution at various temperatures

Temperature ($^{\circ}\text{C}$)	10	0	-10	-15	-20	-30	-40	-80
Dissolution state	Undissolved	Undissolved	Undissolved	Swollen	Good	Good	Good	Good
Solubility $S_a(\%)$	0	0	0	10	85	86	85	80

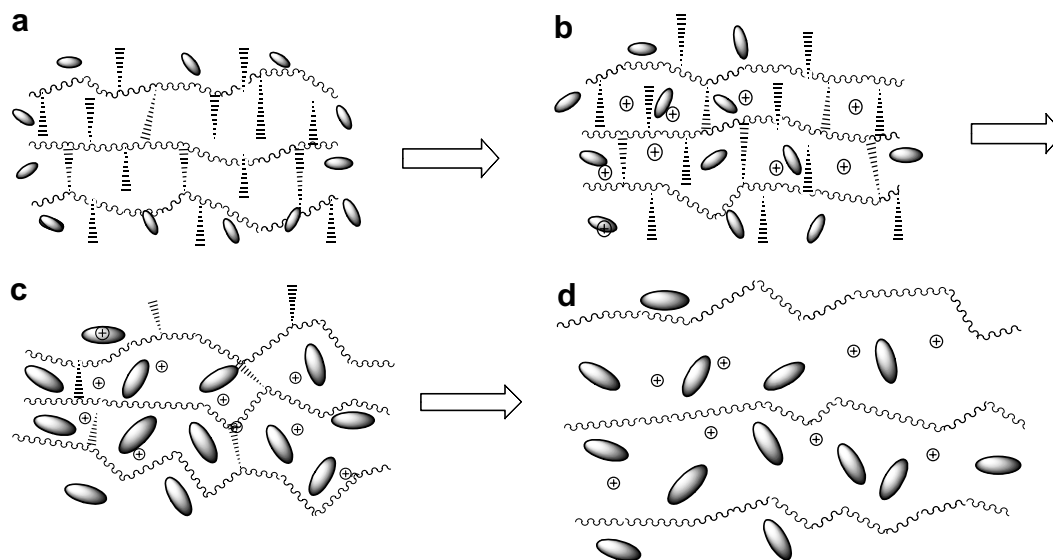


Fig. 1. The diagrammatic illustration of the dissolution process of chitin, including: (a) chitin soaked in 8 wt% NaOH/4 wt% urea aqueous solution at ambient temperature; (b) water molecules enter chitin molecular chain facilitated by the NaOH; (c) water molecules freeze and expand at the freezing temperature, and break the inter- and intra-hydrogen bond; (d) promoting solubility of the chitin. ~~~~~ chitin chain, hydrogen bond, \oplus sodium ion, \bullet water molecular.

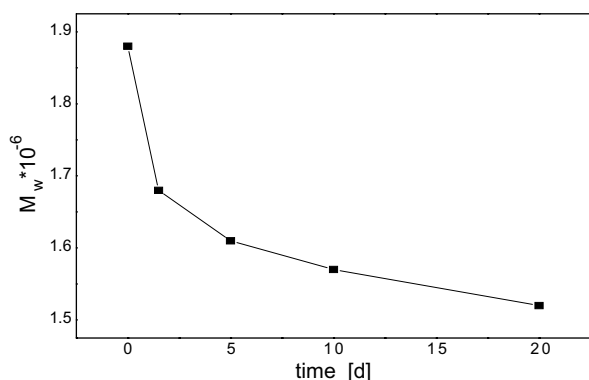


Fig. 2. Effect of the 8 wt% NaOH/4 wt% urea aqueous solvent on the molecular weight of chitin as a function of time.

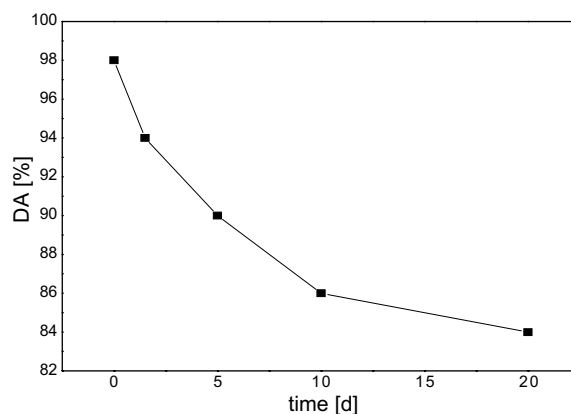


Fig. 3. Effect of the solvent on the degree of acetylation of chitin.

and found that the DD of chitin increased proportionally with increase in the alkali treatment time, and the chitin became soluble in dilute acetic acid at a DD of ca. 28% or over and soluble in water at the DD of ca. 49% (Cho, Jang, Chong, & Ko, 2000). In chitin aqueous solution S8-4-CH2, the degree of acetylation (DA) of chitin decreased rapidly in the beginning of the dissolution process, and then reduced slowly (Fig. 3). The DA of chitin decreased from 0.98 to 0.94 in the beginning of the dissolution process, reducing overall only 4.1% in 36 h. But the DA of chitin reduced from 0.94 to 0.84 (10.6%) in the 20 days storage subsequently. This indicates that the effect of the NaOH/urea solvent on the degree of acetylation of chitin is little, which is less than the effect of NaOH solution previously reported (Einbu et al., 2004. This also illuminates the fact that the addition of urea increases the stability of chitin solution).

3.2.3. FT-IR spectra of chitin

In the FT-IR spectra of the chitin CH0, CH1, CH2 samples (Fig. 4) broad peaks at 3456 cm^{-1} are due to the O–H stretch vibrations and the absorption of intra-hydrogen bonds. The characteristic absorption bands of chitin at about 1628 cm^{-1} (Amide I), 1560 cm^{-1} (Amide II) and 1316 cm^{-1} (Amide III) suggest that the crystal structures of CH0, CH1, CH2 were those of β -chitin. The absorption band of CH1 at about 1560 cm^{-1} (Amide II) is stronger than CH0 and N–H stretch vibration absorption appear at about 3264 cm^{-1} , indicating NaOH/urea aqueous solvent affects the structure of chitin to some extent. The change in infrared spectra was consistent with the results in 3.2.2. The FT-IR spectra of CH1 and CH2 are alike, accounting for the stability of chitin in NaOH/urea aqueous solution. In the FT-IR spectra of CH0, CH1, CH2, the lack of double peaks confirms the β -chitin format and

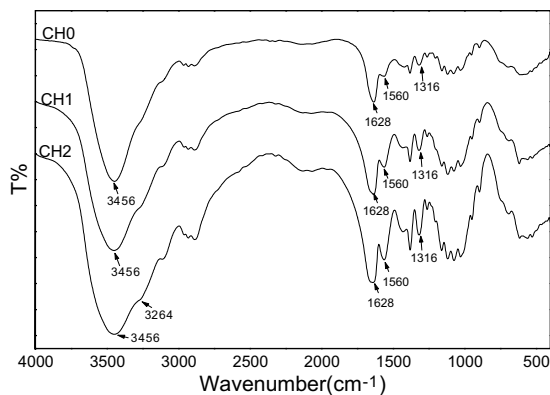


Fig. 4. FT-IR spectra of chitins. CH0, original chitin; CH1, chitin precipitated with 10 wt% H_2SO_4 from 2.0 wt% chitin solution; CH2, chitin precipitated from 2.0 wt% chitin solution which had been kept at -20°C for 5 days.

no crystal conversion from β -chitin to α -chitin (α -chitin, having the structure of an antiparallel chain, is characterized by intersheet and intrasheet hydrogen bonding, and the absorption band for amide I is split. However, β -chitin has intrasheet hydrogen bonding by parallel chain, and the absorption band for amide I is a single peak.), which is different to the treated chitin solution compared with using NaOH alone (Noishiki et al., 2003) and again indicates the addition of urea increases the stability of chitin solution.

3.2.4. X-RD profiles of chitin

In the X-ray diffraction profiles the various chitin samples, two broad crystalline reflections at 9.6° and 19.6° can be observed in the 2θ range of $5\text{--}45^\circ$ (Fig. 5), indicating that CH0 is β -chitin, being congruent with reported values (Cho et al., 2000; Jang, Kong, Jeong, Lee, & Nah, 2004). There are three crystalline reflections at 9.2 , 19.2 and 26.3° in the 2θ range of $5\text{--}45^\circ$ in the X-RD profiles of CH1, in which crystalline reflections at 9.2° , 19.2° are obviously decreased as compared to the case of chitin CH0,

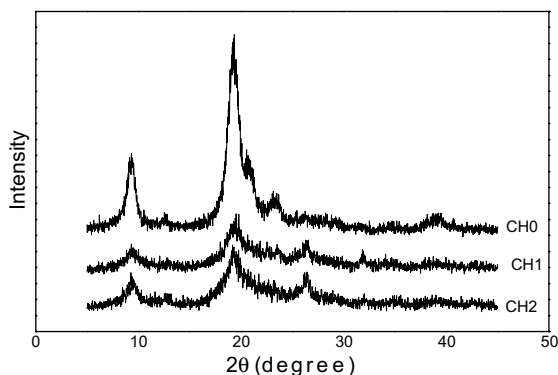


Fig. 5. X-RD profiles of chitin CH0: Original chitin; CH1: Chitin precipitated with 10 wt% H_2SO_4 from 2.0 wt% chitin solution; CH2: Chitin precipitated from 2.0 wt% chitin solution which had been kept at -20°C for 5 days.

suggesting that the crystallinity of chitin decreases in the processing of dissolution and regeneration. But the crystalline reflection at 26.3° increases according to the deacetylation by alkali treatment, which is in agreement with the literature (Feng et al., 2004) and compared with CH0, reflecting the effect of alkali consistent with the results shown in Fig. 4. The X-ray diffraction profile of CH2 is similar to that of CH1, implying the structural stability of chitin in NaOH/urea aqueous solution. The solubility of chitin had a close relationship with its crystal structure and crystallinity.

The insolubility of CH0 is attributed to its high crystallinity, and the solubility improved through the dissolution process (including the low temperature and stirring process) and regeneration as the intra- and inter-molecular hydrogen bonds were weakened thereby inducing reduced crystallinity. The chitin solubility is related to its crystallinity. Chitin cannot be swollen easily because of its high crystallinity. Water molecules enter the chitin molecular chain with the help of NaOH and the cooling to -20°C . The freezing and thawing and then stirring is of benefit for the dissolution of chitin, and expand to break the inter- and intra-hydrogen bonds, which depresses chitin crystallinity and promotes the solubility of chitin (Cho et al., 2000). The results show that the alkali-freezing process reduces the crystallinity of chitin but the effect is limited and not further modified by a prolonged treatment (Feng et al., 2004).

3.3. The rheological behaviors of chitin in NaOH/urea aqueous solution

3.3.1. Steady shear data analysis

The steady shear viscosity dependence in Newtonian plateau on the shear rate of chitin aqueous solution in the range of concentration from 0.5 wt% to 2 wt% in solvent S8-4 at 20°C is given in Fig. 6. Clearly, the rheological behavior of chitin in NaOH/urea aqueous solution was influenced by the concentration chitin. The behavior shows

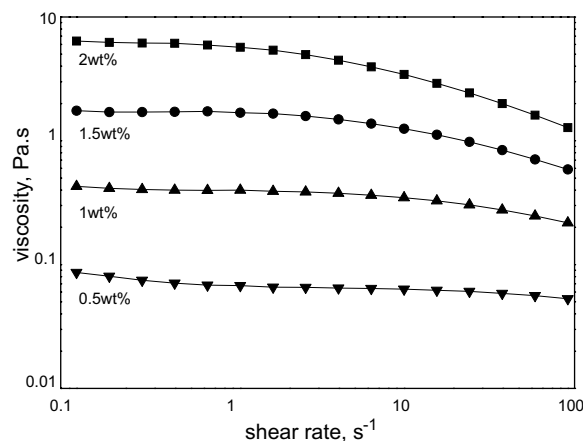


Fig. 6. Dependence of the steady shear viscosity on the shear rate for the chitin solution at different concentrations at 20°C .

a Newtonian behavior of the solutions at high dilution (0.5 wt%, 1.0 wt%), and a shear-thinning rate behavior as the concentration increases. The critical shear rate ($\dot{\gamma}_c$), corresponding to the transition from Newtonian to viscoelastic behavior, moves to lower values with an increase of the concentration, similar to that polysaccharides solutions, such as galactomannan solution. (Kapoor et al., 1998). The zero shear viscosity (η_0) values increase when the concentration rises, and at the same time the Newtonian plateau limit shifts to a lower shear region, similar to that for polysaccharides (Castelain, Doublier, & Lefebvre, 1987; Milas, Rinaudo, & Tinland, 1985). The critical shear rate is about 1 s^{-1} at a concentration of 2 wt%, revealing the chain rigidity of chitin in NaOH/urea aqueous solution.

From dependence of the steady shear viscosity on the shear rate for the chitin solution at different times (Fig. 7), it is noted that the viscosity of chitin solution hardly changed with being kept at low temperature for 72 h, which implies that the stability of chitin solution is good. It is consistent with the results illustrated (Figs. 4 and 5.) that 8 wt% NaOH/4 wt% urea solvent at low temperature adventitiously has little effect on chitin structure.

3.3.2. Gel temperature of chitin in NaOH/urea aqueous solution

Gelation temperature can be defined as the temperature at which G' the dynamic shear storage modulus is equal to G'' the dynamic shear loss modulus, which is related to angular frequency. In this experiment, the temperature when G' is equal to G'' under the condition of $\omega = 1 \text{ rad s}^{-1}$ is regarded as the gelation temperature. It is noted in Fig. 8 that G' is smaller than G'' when the temperature is lower than the gelation temperature, and the lower the concentration, the lower G' and G'' values are. The G' and G'' value increase promptly when temperature is raised to the gelation temperature; moreover G' increases faster than G'' . G' is larger than G'' when the temperature is higher than the gelation temperature as the gel is formed. The gelation

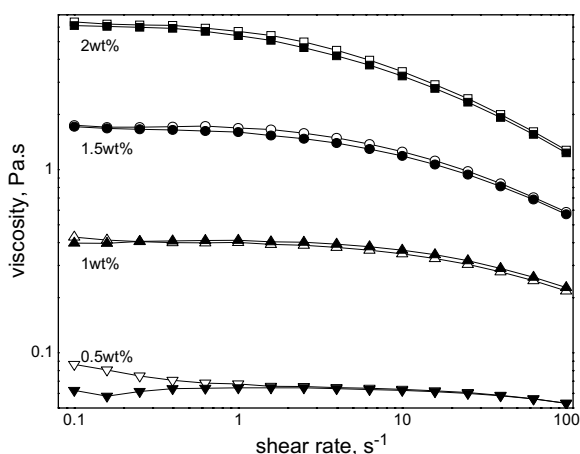


Fig. 7. Dependence of the steady shear viscosity on the shear rate for the chitin solution in different time at 20 °C. Open symbols denote chitin solution just prepared and closed symbols denote chitin solution having been kept at low temperature for 72 h, respectively.

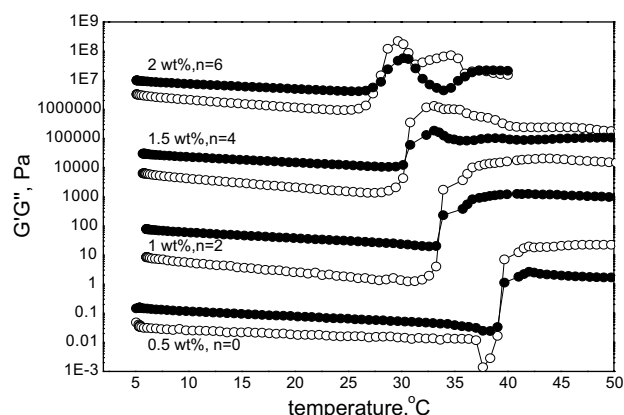


Fig. 8. Temperature dependence of storage modulus G' and loss modulus G'' of chitin in NaOH/urea aqueous solution with different concentrations at a heating rate of 1°C min^{-1} and at a angular frequency of 1 rad s^{-1} . Open and closed symbols denote G' and G'' , respectively. The data is shifted along vertical axes by 10^n with given a value to avoid overlapping.

temperature of 2, 1.5, 1, 0.5 wt% chitin solution are 27.5, 30.5, 33.5, 39.1 °C, respectively, which confirms the lower the concentration is, the higher the gelation temperature is.

The chitin aqueous solution was transparent and stable below gelation temperature. But a white chitin gel was formed when the temperature reached or exceeded the gelation temperature. This chitin gel is a thermosensitive hydrogel and forms rapidly, 1.5 wt% chitin solution becoming transformed into gel after being held at 30 °C for 3 min. The higher the temperature is, the faster the formation speed of the gels is.

4. Conclusions

NaOH/urea aqueous solution was used as a solvent system of chitin for the first time. 8 wt% NaOH/4 wt% urea was regarded as an appropriate solvent and -20°C was confirmed as a suitable treatment temperature. From the viscosity, elemental, FT-IR and X-RD analyses, it was inferred that NaOH urea solvent at low temperature had little effect on chitin structure and that urea is of benefit to the stability of chitin solution. Rheological analyses indicated that chitin aqueous solution in high concentration is a pseudoplastic fluid, and that chitin aqueous solution in low concentration is a Newtonian fluid. This chitin aqueous solution is sensitive to temperature and will transform to a gel when temperature increases. This work is practical and should promote the research on chitin molecular structure and improve the application of chitin, especially in biomedicine.

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