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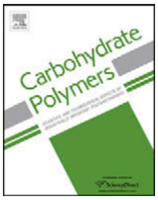

Rheological behaviour of chitin in NaOH/urea aqueous solution

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ABSTRACT

The rheological behaviour of chitin in 8 wt% NaOH/4 wt% urea aqueous medium was evaluated by steady shear and dynamic oscillatory tests, in which the effects of concentration, temperature and time on the rheological behaviour of chitin aqueous solution were investigated in detail. It suggested that chitin aqueous solution is sensitive to temperature, which will transform to a gel when temperature increases to physiological conditions. And the higher the concentration is, the lower the gelation temperature is. The comparison on rheological behaviour of chitin aqueous solution at different time reveals that 8 wt% NaOH/4 wt% urea solvent at low temperature has little effect on chitin structure. It is interesting that the chitin gel has reversibility and it will transit to solution after being treated at low temperature again. The comparison on rheological behaviour between the original chitin aqueous solution and the chitin aqueous solution after gelation reveals that gelation has a little effects on solution properties.

1. Introduction

Chitin is the second most abundant form of polymerized carbon found in nature, which is biorenewable, biocompatible, environmental friendly, biodegradable and biofunctional, proving 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).

But chitin is not widely used by the pharmaceutical industry at present because of its poor solubility characteristics. Chitin is insoluble in dilute aqueous solvents and common organic solvents, because of its strong interchain hydrogen bonds. Various attempts have been made to improve the solubility of chitin while retaining its molecular structure. Its main solvents are chlorohydrin/inorganic acid; LiCl/DMF; LiCl/DMAc; LiCl/NMP; very strong acid; and 40% NaOH (Austin, 1975), which fall short of requirements in terms of non-toxicity, zero pollution, non-depolymerization and low cost. Plenty of researches revealed that frozen alkali chitin has already been chosen as a convenient precursor for efficient modifications (Hirano, 1988; Tokura & Tamura, 2001). Chitin can be dissolved when an alkaline suspension of the polymer is mixed with ice. An interesting study by Feng, Liu, and Hu (2004) concerning the influence of alkali-freezing treatment on the solid state structure of chitin showed that this could be a suitable state of chitin for further modificatiton. Dilute solution properties of chitin of various molecular weights in alkali have been determined, showing that alkali is a good solvent (Einbu, Naess, Elgsaeter, & Vårum, 2004). Recently, chitin was well dissolved (Hu et al., 2007). It was inferred that 8 wt% NaOH/4 wt% urea solvent at low temperature adventitiously had little effect on chitin structure and the urea was beneficial to the stability of chitin solution.

Novel solvent of chitin is currently the key to its further research and application, which makes for obtaining new types of chitin fibre through spinning such solutions. The rheological properties of a spinning solution are very important factors for spinnability. Chen, Sun, and Zhang (2004) used an advanced rheometric expansion system to investigate rheological properties of 1, 2 and 3 wt% chitin/LiCl-DMAc solutions for the purpose of improving the properties of chitin fibre. The results from steady rheological testing showed that the 1, 2 and 3 wt% chitin/LiCl, DMAc solutions were non-Newtonian fluids. Their apparent viscosities, and observations from the appearances and polarized optical microscope, showed that the 2 and 3 wt% chitin/LiCl, DMAc solution formed lyotropic liquid crystals, whereas the 1 wt% did not, which implied that the 2 wt% chitin/LiCl, DMAc liquid crystals should had best spinnability and gave best quality of fibre after spinning among the three solutions. Dynamic measurements on the 3 wt% chitin/LiCl, DMAc solution showed that the changes in its viscous and elastic properties with temperature were different from those of common

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polymer solutions (Chen et al., 2004). Rheological properties of chitin, cellulose, and their mixtures dissolved in a common solvent showed that mixtures with comparable polymer concentrations exhibited negative deviations from additivity with respect to viscosity and the activation energy of viscous flow, which was related to a microheterogeneity of the system. The system comprising a small additive of one polymer to another is more homogeneous than the solutions of individual polymers, of which the mechanism was unknown. But the sorption by the films of one polymer containing 0.5–2.5% other component was confirmed through the negative values of the Flory–Huggins parameters (Nud'ga et al., 1999).

Determination of the rheological properties of a solution is a convenient and effective way, which gains fundamental knowledges of the spinnability and structure–property relationships for a spinning solution. Given the new aqueous solvent of chitin (Hu et al., 2007), in the current work, the rheological behaviour of the chitin aqueous solution was evaluated by rheological analysis for the first time.

2. Materials and methods

2.1. Materials

Chitin was gained from crab shell, purchased from Dalian Xindie Chitin Co. Ltd., Dalian, China, shifted to maximum particle size of 0.635 mm diam. The viscosity-average molecular weight was determined as 1.88×10^6 using a 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. Preparation of chitin NaOH/urea aqueous solution

Chitin NaOH/urea aqueous solution was prepared as reported (Hu et al., 2007). Chitin powder (4 g) was dispersed in 8 wt% NaOH/4 wt % urea aqueous solvent (200 g, solvent coded as S8-4). The suspensions were maintained at −20 °C and stirred twice in 36 h. The chitin solutions were centrifuged at $3500 \times g$ at 10 °C for 20 min and 2.0 wt% chitin aqueous solution was prepared (coded as chitin solution S8-4-CH2).

2.3. Rheological measurement

The chitin solution S8-4-CH2 was diluted with the solvent S8-4 to prepare 1.5, 1.0 and 0.5 wt% chitin solutions, which were coded as S8-4-CH1.5, S8-4-CH1 and S8-4-CH0.5, respectively. The chitin solutions S8-4-CH1.5, S8-4-CH1 and S8-4-CH0.5 were transformed to gels at 40 °C, and then maintained at −20 °C for 12 h, coded as S8-4-CH1.5-1, S8-4-CH1-1 and S8-4-CH0.5-1. S8-4-CH1-1 was treated again and coded as S8-4-CH1-2.

The chitin solutions with concentration range from 0.5% to 2% were characterized for their rheological properties using the steady shear and dynamic oscillatory tests. All rheological measurements were performed on a Rheometric Scientific ARES controlled strain rheometer (TA Instruments, New Castle, DE, USA). The rheometer was equipped with two sensitive force transducers for torque measurements ranging from 0.004 to 100 g cm and a thermo-bath with circulating water that was calibrated to give a temperature in the sample chamber within ±0.5 °C of the set value. A Couette (two concentric cylinders) cell geometry was used for monitoring the steady-state shear flow and dynamic rheology of the samples modulus. The degassed solution of 10 mL was heated or cooled to desired temperature directly in the rheometer (without shearing or oscillating) and then covered with mineral oil in order to prevent evaporation during the measurements.

The steady shear viscosities of solutions S8-4-CH1.5, S8-4-CH1, S8-4-CH0.5, S8-4-CH1.5-1, S8-4-CH1-1 and S8-4-CH0.5-1 were determined rheometrically at 20 °C, angular frequency, 1 rad s^{-1}, rate 0–100 s^{-1}. The gelation temperature of the solutions S8-4-CH2, S8-4-CH1.5, S8-4-CH1, S8-4-CH0.5, S8-4-CH1-1 and S8-4-CH1-2 was determined rheometerically: angular frequency, 1 rad s^{-1}; temperature range, 5–50 °C. For the temperature sweep measurement to determine the gelation temperature, oscillatory measurements were performed while the temperature was increased at the rate of 1 °C/min between 5 and 50 °C. The gelation time of the S8-4-CH2, S8-4-CH1.5, S8-4-CH1 and S8-4-CH0.5 solutions was determined rheometrically at 20, 30 and 40 °C; angular frequency, 1 rad s^{-1}. For the time sweep measurement, it was defined as time $t = 0$ s when the temperature reaches the desired temperature. The gelation frequency of the S8-4-CH2, S8-4-CH1.5, S8-4-CH1 and S8-4-CH0.5 solutions was determined rheometrically at 20, 30 and 40 °C; angular frequency range, 1–100 rad s^{-1}. The sweep of the frequency (ω) ranged from 0.1 to 100 rad s^{-1}, and each frequency sweep took 900 s to complete. So the dynamic viscoelastic functions such as the dynamic shear storage modulus (G') and loss modulus (G'') were measured as a function of temperature, time or angular frequency. 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 s^{-1}) to determine zero-shear viscosities. It showed that all the solutions exhibited linear viscoelastic behaviour at 1 Hz with a constant shear strain 100–400%.

2.4. Morphological studies

Scanning electron microscopy was performed on hydrogels (freeze-dried to maintain the porous structure without any collapse) to obtain information on the pore structure of hydrogels. Then they were plunged into liquid nitrogen and the vitrified samples were cut with a cold knife. The samples were mounted on the base plate and coated with gold. The morphology was investigated using a Hitachi (Tokyo, Japan) S-570 scanning electron microscopy.

3. Results and discussion

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

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 aqueous chitin solution in NaOH/urea was homogeneous and transparent as reported previously (Hu et al., 2007).

3.2. The rheological behaviour of chitin in NaOH/urea aqueous solution

3.2.1. Steady shear and dynamic frequency sweep data analysis on chitin aqueous solution

The steady shear viscosity dependence on the shear rate of chitin aqueous solution in solvent S8-4 at different concentrations and times has been discussed in our previous work (Hu et al., 2007). The rheological behaviour of chitin in NaOH/urea aqueous solution was influenced by the chitin concentration, which suggested that chitin aqueous solution at high concentration is pseudoplastic fluid while chitin aqueous solution at low concentration is Newtonian fluid. The comparison on rheological behaviour of chitin aqueous solution at different times revealed that 8 wt% NaOH/4 wt% urea solvent

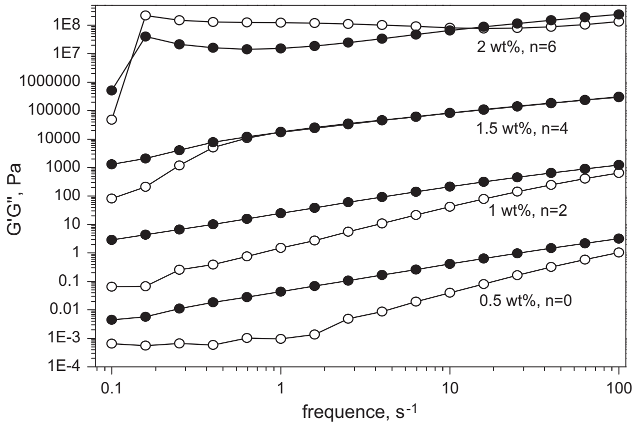

Fig. 1. Frequency dependence of storage modulus G' and loss modulus G'' of chitin aqueous solutions with different concentrations at 30 °C. Open and closed symbols denote G' and G'', respectively. The data are shifted along vertical axis by 10^n with a given value to avoid overlapping.

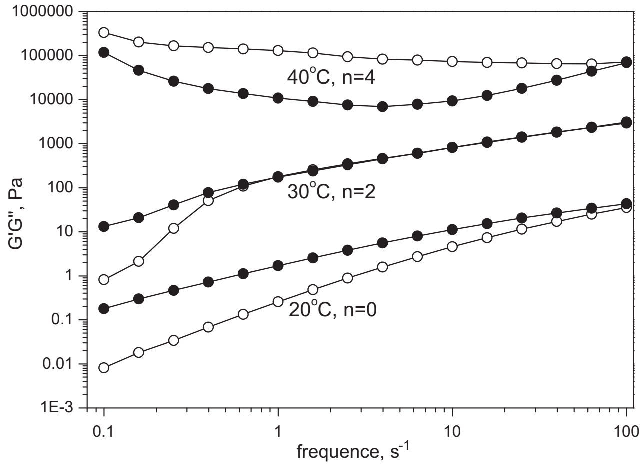

Fig. 2. Frequency dependence of storage modulus G' and loss modulus G'' of 1.5 wt% chitin solution at different temperatures. Open and closed symbols denote G' and G'', respectively. The data are shifted along vertical axis by 10^n (n value is 0, 2, 4 respectively, which is added to shift the G' and G'' curves to avoid overlapping).

at low temperature hardly affected chitin structure. Furthermore, dynamic frequency sweep was discussed below.

Frequency sweep information can be used to characterize or classify dispersed systems. The four common and traditional classifications are that of a dilute solution, an entanglement network system (or a concentrated solution), a weak gel and a strong gel. Fig. 1 shows the plot of G', G'' vs. frequency for the chitin aqueous solution at 30 °C. The lower is the concentration of chitin solution, the smaller the G' value and the lower gel intensity are. A dilute solution shows loss modulus G'' is larger than storage modulus G' over the entire frequency range, yet the moduli G'' and G' values tend to increase and approach each other with increasing frequencies, which comes into being an entanglement network system that G'' and G' curves intersect at the middle of the frequency range (Clark & Ross-Murphy, 1987).

The magnitudes of G' are lower than those of G'' at 30 °C for 1, 0.5 wt % chitin solution. This type of behaviour is indicative of a dilute solution according to the classification mentioned above. The gelation temperatures of 1 and 0.5 wt % chitin solution are higher than 30 °C, which is consistent with the result in Section 3.2.2. The magnitudes of G' are lower than those of G'' at 30 °C for 1.5 wt % chitin solution when frequency is lower than $1\,\mathrm{s}^{-1}$, which is indicative of a dilute solution. And the magnitudes of G' are equal to those of G'' at 30 °C for 1.5 wt% chitin solution when frequency is higher than $1\,\mathrm{s}^{-1}$, which indicates its gelation temperature is 30 °C. The magnitudes of G' are higher than those of G'' at 30 °C for 2 wt % chitin solution when frequency is lower than $10\,\mathrm{s}^{-1}$, which is indicative of a weak gel. The magnitudes of G' and G'' intersect at 30 °C for 1.5 wt% chitin solution when frequency is $10\,\mathrm{s}^{-1}$, which indicates its gelation temperature is lower than 30 °C. However, the term “liquid-like” solution seems more appropriate, because the separation between G'' and G' values tends to increase with decreasing polymer concentration and the moduli at the same frequency increased with increasing concentration. It has been reported that an entanglement network system shows G'' and G' curves intersecting at the middle of the frequency range indicating a clear tendency for more solid like behaviour at higher frequencies (Xu, Liu, & Zhang, 2006). Weak gels have G' higher than G'' with moduli almost parallel to each other. Strong gels also have G' higher than G''; however, G' has a slope of 0, and G'' displays a minimum at intermediate frequencies (Clark & Ross-Murphy, 1987).

The frequency dependence of the viscoelastic properties of 1.5 wt% chitin solution and the gel intensity might be attributed to the different gelation temperatures (Fig. 2), in which the G' and G'' are measured as a function of the frequency from 0.1 to 100 Hz. When the ambient temperature is 20 °C, largely lower than the gelation temperature, the viscous modulus G' is lower than the elastic modulus G'' within the frequency range. Those features are characteristic of the stable viscous liquid, which indicates its gelation temperature is higher than 20 °C. With an increase of the temperature close to the gelation temperature, the difference between G' and G'' becomes small, that is close to gelation. Furthermore, G' increases gradually to exceed G'' when the ambient temperature is 30 °C that is equal to or even lightly higher than the gelation temperature. It means the weak gel has been formed. However, the further increase of frequency causes a significant decrease in storage modulus, which is indicative of structure break by mechanical shear. The storage modulus becomes lower than the loss modulus and the system behaves like a solution. The rheological behaviour of 1.5 wt% chitin solution at 30 °C is typical of a “weak gel”, which has the frequency dependence. At last, when the ambient temperature is 40 °C, obviously higher than the gelation temperature, G' is always higher than G'' over the whole frequency range. It is evident that the elastic modulus G' shows almost no dependence on frequency. These features are characteristic of a “strong gel”, of which G' has a slope of 0, and G'' displays a minimum at intermediate frequencies (Clark & Ross-Murphy, 1987).

3.2.2. *Gelation of chitin in NaOH/urea aqueous solution*

Chitin in NaOH/urea aqueous solution is sensitive to temperature. It is transparent and stable below 20 °C and will transform to a white gel when temperature increases to physiological conditions. The gelation temperatures of 2, 1.5, 1, and 0.5 wt% chitin solutions were 27.5, 30.5, 33.5, and 39.1 °C respectively as reported previously (Hu et al., 2007), which showed that the gelation temperature decreased with an increase of the chitin concentration. This implies that elevating the concentration increases the chance of collision of the chitin chains.

Gelation time is defined as the time when the storage modulus becomes higher than the loss modulus. It reflects the changes of G' and G'' during the gelation process, indicating the gelation speed and the gel intensity. There are many factors that have effects on gel time for chitin hydrogel, such as environmental temperature and chitin solution concentration.

The gelation processes at different temperatures for 1 wt% chitin solution are different (Fig. 3). At any temperature slightly lower than the gelation temperature, which is about 33.5 °C, gelation could take place as long as enough time was given. Therefore, the gel is only formed in several minutes when the experiment tem-

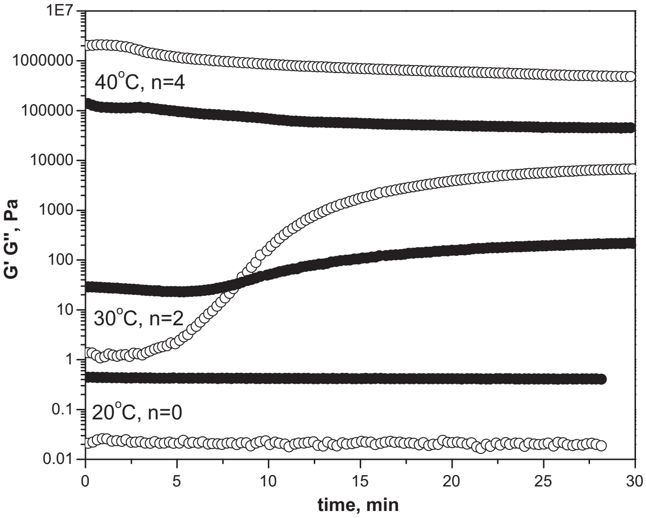

Fig. 3. Time dependence of storage modulus G' and loss modulus G'' of 1 wt% chitin solution for different temperatures at a frequency of 1 rad/s. Open and closed symbols denote G' and G'', respectively. The data are shifted along vertical axis by 10^n (n value is 0, 2, 4 respectively, which is added to shift the G' and G'' curves to avoid overlapping).

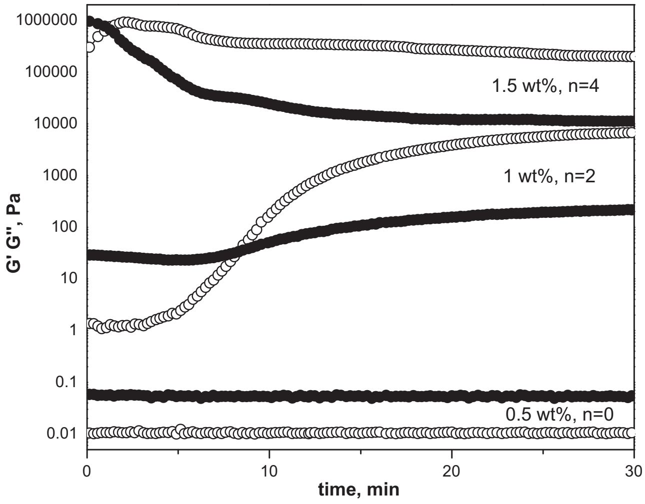

Fig. 4. Time dependence of storage modulus G' and loss modulus G'' of chitin solution for different concentrations at 30 °C and at a frequency of 1 rad/s. Open and closed symbols denote G' and G'', respectively. The data are shifted along vertical axis by 10^n with a given value to avoid overlapping.

perature is 30 °C which is close to the gelation temperature. The gel forms very quickly when the experiment temperature is elevated to 40 °C. The higher the temperature is, the faster the formation speed of the gel is.

During the gelation process, both G' and G'' increase gradually and eventually reach the onset of a plateau, in which G' is largely higher than G''. This indicates that the elastic response of the material is stronger than the viscous response. The present hydrogel system displays a predominantly solid-like behaviour. As known, the storage modulus can be considered as a measure of the extent of gel network formation. The higher G' value of the gel at the higher temperature means the stronger gel intensity. It has been explained that raising the temperature causes some macromolecules or some sections of macromolecules to dump into lumps of a polymer-rich phase, where there are always interactions of hydrophobic groups (Cabane, Lindell, Engstrom, & Lindman, 1996).

The time dependence of storage modulus G' and loss modulus G'' of chitin solutions for different concentrations showed that the influence of chitin concentration on the gelation process (Fig. 4). With an increase of chitin concentration from 0.5 to 1.5 wt% at 30 °C, the gelation time decreases and gel intensity is enhanced. These results are consistent with the gelation mechanism (Section 3.3). The chitin is responsible for the hydrophobic interactions at high temperature. When its concentration increases, the entanglements among chitin chains are heightened leading to the increase on the gel intensity. When concentration is barely above the sol/gel point, a gel exhibit aging and its G' and G'' decline rather than increase with time, accompanied by a reversal from the sol/gel state back to the sol state. This is an uncommon aging behaviour for a polysaccharide and a detailed explanation is provided in the literature (Rwei, Chen, & Cheng, 2005).

3.2.3. *The reversibility of chitin gel*

Chitin aqueous solution will transpose to chitin gel when the environmental temperature reached or exceeded the gelation temperature. It is interesting that the chitin gel has reversibility and it will transpose to solution after being treated at −20 °C for 24 h, which is different from cellulose (Cai & Zhang, 2006). Fig. 5 shows the comparison on the steady shear viscosity for the chitin solution before and after gelation at 20 °C. For 0.5 wt% chitin solution, the viscosities of chitin solution decreased a little after gelation and dissolution. For 1 wt% chitin solution, the viscosities of chitin solution hardly changed after gelation and dissolution. But for 1.5 wt% chitin solution, the viscosities of chitin solution increased obviously after gelation and dissolution, which displayed a shear-thinning rate behaviour of high concentration solution. For 2 wt% chitin solution, the viscosity of chitin solution after gelation and dissolution was too high to be measured. It is noted that gelation treatment partly influences the chitin solution at high concentration, whereas it hardly influences the chitin solution at low concentration. It is implied that the association between chitin moleculars and solvent moleculars improves and the solubility of chitin solution increases a certain extent after gelation treatment.

The comparison on the gelation temperature of 1 wt% chitin solution before and after gelation shows the effect of gelation on chitin molecules (Fig. 6.). The gelation temperature was 32 °C after gelation once and 31 °C after gelation twice while the gelation temperature was 33.5 °C for the first gelation. It indicates that the gelation temperature of chitin solution declined slightly and the rate of gelation increased after gelation treatment. The comparison of rheological behaviour of chitin aqueous solution before gelation and after gelation reveals that gelation has a little effect on solution properties. The association between chitin molecules and

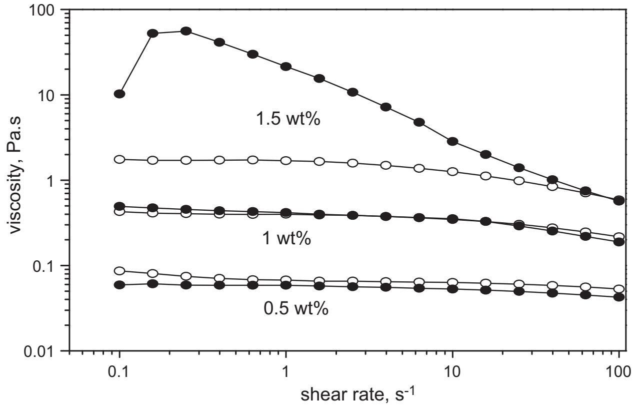

Fig. 5. Dependence of the steady shear viscosity on the shear rate for the chitin solution before and after gelation at 20 °C. Open symbols denote chitin solution just prepared and closed symbols denote chitin solution after gelation, respectively.

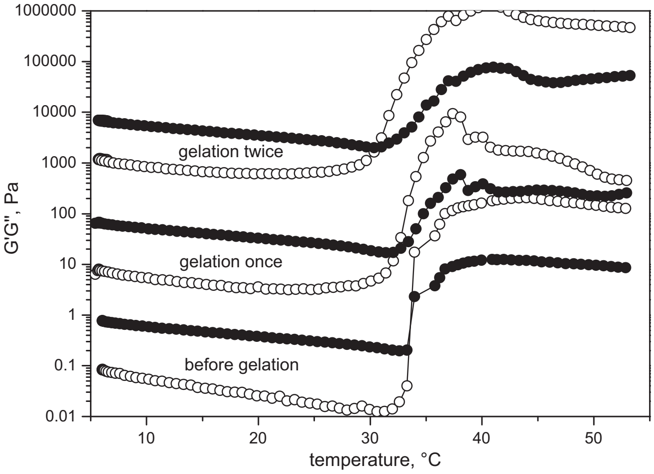

Fig. 6. Temperature dependence of storage modulus G' and loss modulus G'' of 1 wt% chitin in NaOH/urea aqueous solution before and after gelation at a heating rate of 1 °C min^{-1} and at a angular frequency of 1 rad s^{-1}. Open and closed symbols denote G'' and G'', respectively. The data are shifted along vertical axis by 10^n with given a value to avoid overlapping.

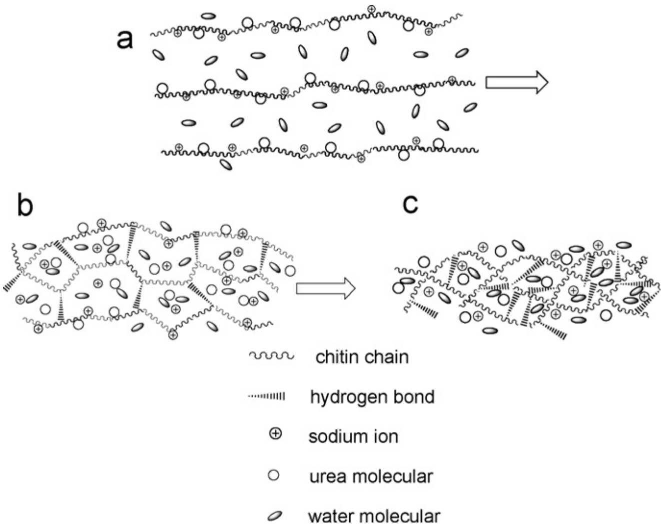

Fig. 7. The diagrammatic illustration of the gelation process of chitin, including: (a) Chitin in solution state at low temperature. (b) Chitin in turbid state slightly lower than the gelation temperature. (c) Chitin in gel state above gelation temperature.

solvent moleculars is improved after gelation treatment, which is consistent with the results illustrated in Fig. 5.

3.3. The mechanism of chitin gel formation

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. The thermally induced gel from the random association of concentrated chitin solutions in 8 wt% NaOH/4 wt % urea was successfully prepared. The chitin hydrogel was formed by adjusting the environmental temperature from 10 °C to 30 °C. The temperature was controlled at 10 °C when the chitin solution was prepared. The 1.5 wt% chitin solution was still transparent after being treated at 10 °C for 72 h. When the chitin solution was placed at 30 °C, it transformed into a semi-transparent elastomer after one minute. The high temperature can reduce the intermolecular hydrogen bonding interactions and accelerate the mobility of chitin molecules. So the energized solvent molecules surrounding the chitin chains are removed. The dewatered hydrophobic chitin chains associate with each other. As a result, a chitin gel is formed. This type of thermosensitive gelation has also been observed in other cases (Bhattaraim, Ramay, Gunn, Matsen, & Zhang, 2005; Chenite et al., 2000; Tang, Du, Hu, Shi, & Kennedy, 2006). This chitin gel is a thermosensitive hydrogel and forms rapidly. The higher the temperature is, the faster the formation of the gel is.

On the basis of the rheometric information, a schematic process describing the formation of the gel in the chitin solution (Fig. 7) illustrates the mechanism of the thermosensitive sol–gel transition for the chitin solution. There are strong intra- and inter-molecular hydrogen bonds in chitin, and the self-association tendency of hydroxyl on the chitin chain is much larger than association between chitin and water molecules, so chitin is insoluble in water. But sodium ions, water, and urea molecules could form an overcoat surrounding the chitin chain to prevent its self-association, resulting in the chitin to be water soluble (Hu et al., 2007). At a low temperature, the solution was relatively stable because the self-association was prevented by the formation of an "overcoat" structure. As shown in Fig. 7a, the chitin chains were surrounded with small molecules such as urea and NaOH, as if covered with an overcoat, and dispersed in the aqueous solution at a molecular level at low temperature. At the same time, the low temperature can also reduce the mobility of chitin molecules, which further prevents the association of chitin chains. It is thus a poor conformation or shape to build up a three-dimensional network structure because of the difficulty of creating contacts between the junction chains.

When temperature is elevated, the overcoat layer is broken because of the rapid thermal escape motion of small molecules, which exposes the hydroxyl groups of the chitin to each other. The random junction between the chitin molecules occurred on the same chains. The formation of thermally induced gel involves the association of chain segments, which results in a three-dimensional network that contains solvent in the interstices. And the physical cross-linking networks wrapping water molecules were formed by the self-association force of the chitin macromolecules, leading to turbidity of the solution (Fig. 7b). This type of thermosensitive gelation has also been observed in other cases (Weng, Zhang, Ruan, Shi, & Xu, 2004).

When temperature is higher than gelation temperature, a number of junction points of chitin chains occurred to form randomly cross-linked networks. This results in a transition from the solution to the gel state as shown in Fig. 7c, indicating that the gelation results from a physical interaction. In this case, the exposed hydroxyl groups of chitin play an important role in the formation of the cross-link network structure by random self-association of chitin chains. The self-association is weak at a relatively low temperature as a result of the shield effect of the overcoat, but it is strengthened at the elevated temperatures, leading to further aggregation to form gels. Therefore, the self-association tendency of chitin is assumed to be the main driving force in the formation of gel.

3.4. Scanning electron microscopy

Determination of the freeze-dried chitin gel by scanning electron microscopy shows that its morphology is asymmetric network (Fig. 8). The section plane morphology of the chitin gel is shown in Fig. 8a and clearly illustrates that the chitin hydrogel network is evident, which is mainly due to an increase of continuous networks formed through many entanglements when the temperature increases. The former SEM micrograph indicates the porous structure is asymmetric and the pore size on the surface is smaller than the one in the middle. Fig. 8b clearly shows the microstructure of chitin gel surface is compact and smooth.

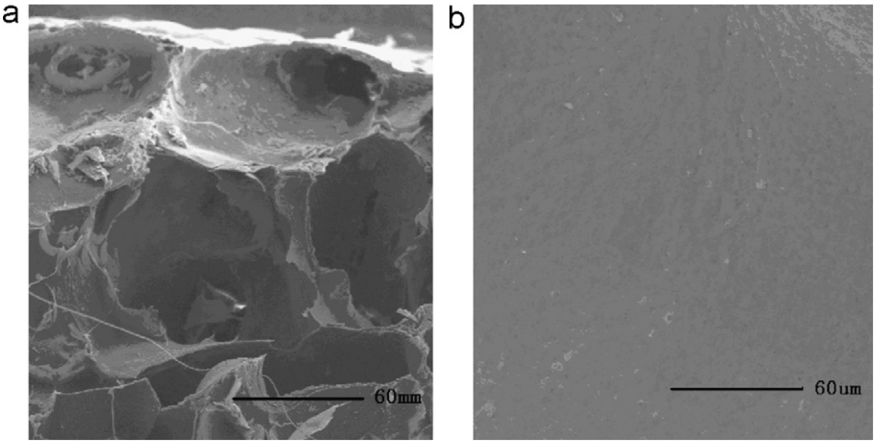

Fig. 8. SEM of chitin gel (a, section; b, surface).

4. Conclusions

The rheological behaviour of the chitin aqueous solution in 8 wt% NaOH/4 wt% urea was evaluated by rheological analysis for the first time, and the effects of concentration, temperature and time on the rheological behaviour of chitin aqueous solution were investigated detailedly. It suggests that chitin aqueous solution at high concentration is pseudoplastic fluid while chitin aqueous solution at low concentration is Newtonian fluid. The comparison on rheological behaviour of chitin aqueous solution at different time reveals that 8 wt% NaOH/4 wt% urea solvent at low temperature hardly affects chitin structure. This chitin aqueous solution is sensitive to temperature. It is transparent and stable below 20 °C and will transform to a white gel when temperature increases to physiological conditions. And the higher the concentration is, the lower the gelation temperature is. It is interesting that the chitin gel has reversibility and it will transit to solution after being treated at low temperature. The comparison on rheological behaviour of chitin aqueous solution before and after gelation reveals that gelation has a little effects on solution properties. This work is practical and useful, which gains fundamental knowledges of the spinnability and will lead to the spinning of chitin through the 8 wt% NaOH/4 wt% urea aqueous solvent.

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References

Austin, P. R. (1975). U.S. Patent 3,879,377, Chemistry Abstract, 83, P117557s.

Bhattaraim, N., Ramay, H. R., Gunn, J., Matsen, F. A., & Zhang, M. Q. (2005). PEG-grafted chitosan as an injectable thermosensitive hydrogel for sustained protein release. *Journal of Controlled Release*, *103*, 609–624.

Cabane, B., Lindell, K., Engstrom, S., & Lindman, B. (1996). Microphase separation in polymer + surfactant systems. *Macromolecules*, *29*, 3188–3197.

Cai, J., & Zhang, L. N. (2006). Unique gelation behavior of cellulose in NaOH/urea aqueous solution. *Biomacromolecules*, *7*, 183–189.

Chen, L. Y., Du, Y. M., Wu, H. Q., & Xiao, L. (2002). Relationship between molecular structure and moisture-retention ability of carboxymethyl chitin and chitosan. *Journal of Applied Polymer Science*, *83*, 1233–1241.

Chen, B. Q., Sun, K., & Zhang, K. B. (2004). Rheological properties of chitin/lithium chloride, N,N-dimethyl acetamide solutions. *Carbohydrate Polymers*, *58*, 65–69.

Chenite, A., Chaput, C., Wang, D., Combes, C., Buschmann, M. D., Hoemann, C. D., et al. (2000). Novel injectable neutral solutions of chitosan form biodegradable gels in situ. *Biomaterials*, *21*, 2155–2161.

Clark, A. H., & Ross-Murphy, S. B. (1987). Structural and mechanical properties of biopolymer gels. *Advances in Polymer Science*, *83*, 57–192.

Einbu, A., Naess, S. N., Elgsaeter, A., & Vårum, K. M. (2004). Solution properties of chitin in alkali. *Biomacromolecules*, *5*, 2048–2054.

Feng, F., Liu, Y., & Hu, K. (2004). Influence of alkali-freezing treatment on the solid state structure of chitin. *Carbohydrate Research*, *339*, 2321–2324.

Hirano, S. (1988). Water-soluble glycol chitin and carboxymethyl chitin. *Methods in Enzymology*, *161*, 408–410.

Hu, X. W., Du, Y. M., Tang, Y. F., Wang, Q., Feng, T., Yang, J. H., et al. (2007). Solubility and property of chitin in NaOH/urea aqueous solution. *Carbohydrate Polymers*, *70*, 451–458.

Nud'ga, L. A., Petrova, V. A., Bochek, A. M., Kalyuzhnaya, L. M., Alekseev, V. L., Evmenenko, G. A., et al. (1999). Structure of chitin–cellulose mixtures in solution and in the solid state. *Vysokomolekulyarnye Soedineniya Seriya A & Seriya B*, *41*(11), 1786–1792.

Poirier, M., & Charlet, G. (2002). Chitin fractionation and characterization in N,N-dimethylacetamide/lithium chloride solvent system. *Carbohydrate Polymers*, *50*, 363–370.

Rwei, S. P., Chen, I. Y., & Cheng, Y. Y. (2005). Sol/gel transition of chitosan solutions. *Journal of Biomaterials Science-Polymer Edition*, *16*(11), 1433–1445.

Tang, Y. F., Du, Y. M., Hu, X. W., Shi, X. W., & Kennedy, J. F. (2006). Rheological characterisation of a novel thermosensitive chitosan/poly (vinyl alcohol) blend hydrogel. *Carbohydrate Polymers*, *67*, 491–499.

Tokura, S., & Tamura, H. (2001). O-Carboxymethyl-chitin concentration in granulocytes during bone repair. *Biomacromolecules*, *2*, 417–421.

Weng, L. H., Zhang, L. N., Ruan, D., Shi, L. H., & Xu, J. (2004). Thermal gelation of cellulose in a NaOH/thiourea aqueous solution. *Langmuir*, *20*, 2086–2093.

Xu, J., Mccarthy, S. P., Gross, R. A., & Kaplan, D. L. (1996). Chitosan film acylation and effects on biodegradability. *Macromolecules*, *29*, 3436–3440.

Xu, X. J., Liu, W., & Zhang, L. N. (2006). Rheological behavior of *Aeromonas* gum in aqueous solutions. *Food Hydrocolloids*, *20*, 723–729.