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Carbohydrate Polymers 58 (2004) 65–69

Carbohydrate Polymers

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# Rheological properties of chitin/lithium chloride, *N*,*N*-dimethyl acetamide solutions

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Received 25 January 2004; revised 25 April 2004; accepted 25 June 2004

**Abstract**

Rheological properties of 1, 2 and 3 wt% chitin/lithium chloride (LiCl), *N*,*N*-dimethyl acetamide (DMAc) (one part of LiCl in 20 parts of DMAc by mass) solutions were investigated using an advanced rheometric expansion system 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 with shear-thinning behaviour. The 2 wt% chitin/LiCl,DMAc solution formed lyotropic liquid crystals, as determined from the decreased apparent viscosity in contrast to the 1 wt% chitin/LiCl,DMAc common solution. The results also implied that the 2 wt% chitin/LiCl,DMAc liquid crystals should have best spinnability and give best quality of fibre after spinning among the three solutions. The 3 wt% chitin/LiCl,DMAc solution had a similar appearance to the 2 wt% chitin/LiCl,DMAc liquid crystals. 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 common polymer solutions, in that the first normal stress difference could be negative and higher temperature could give higher viscosity. These findings suggested the existence of liquid crystals in the 3 wt% chitin/LiCl,DMAc solution.

*Keywords:* Chitin solution; Rheological property; Lyotropic liquid crystal

## 1. Introduction

Chitin is an abundant natural bio-degradable polymer, with excellent bio-compatibility, non-toxicity and wound healing properties, so it has been widely applied in medical and healthcare fields for applications such as release capsules for drugs, man-made kidney membranes, anti-coagulants and immunity accelerants (Cho, Cho, Chung, Yoo, & Ko, 1999; Matsuyama, Kitamura, & Naramura, 1999; Muzzarelli, 1977, 1993; Okamoto et al., 2002; Onishi, Nagai, & Machida, 1997; Tokura et al., 1990). Also, owing to its relatively high strength and modulus, chitin fibre has been used as surgery sutures, wound dressings and artificial skins (Hirano, Zhang, Chung, & Kim, 2000; Liu & Wu, 1994; Su et al., 1999; Wu & Wu, 1997).

Fibre-reinforced polymeric composites form one of the most important classes of composite and are applied in many fields (Shierrdon, 1989). Our work therefore seeks to prepare chitin fibre not only for its own medical applications but also as a reinforcement filler for polymer matrices. The properties of the fibre-reinforced composites are largely dependent on the characteristics of the fibre, such as its strength, length, the length distribution, diameter, the shape of the interface, and irregularity of surfaces (Dong, 1981). This work aims to enhance the properties of chitin fibre.

Since the tensile modulus of the fibre spun from liquid crystal solutions is at least double of the fibre derived from common wet spinning methods, the former method is often preferable (Dong, 1981). Chitin can be dissolved in few solvents (Austin, 1977, 1984), among which dichloroacetic acid (DCA) was claimed to make chitin form lyotropic liquid crystals by Dong and Wang (1999), but our previous work (Chen, Sun, Fan, & Zhang, 2002) on DCA did not identity this phenomenon. The mixture of lithium chloride (LiCl) and *N*,*N*-dimethyl acetamide (DMAc)

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0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.06.030

(one part of LiCl in 20 parts of DMAc by mass) is one of the best solvents for chitin and it has been extensively used in this context (Austin; Poirier & Charlet, 2002; Striegel, 1997). Our work therefore used this solvent system with the aim of obtaining lyotropic liquid crystals under appropriate preparation conditions. Understanding the rheological properties of a solution is a convenient and effective way to gain a fundamental knowledge of the spinnability and structure–property relationships for the spinning solution. Thus, this work investigates the rheological properties of chitin/LiCl,DMAc solutions in some detail.

## 2. Experimental details

Chitin was kindly supplied by Dong Hua University (Shanghai, China). Its molecular weight was deduced as $5.6\times10^5$ from the intrinsic viscosity of a chitosan solution, as described in our previous work (Chen et al., 2002). Chitin was purified according to established literature methods (Lu & Cao, 1993; Wang, Qin, & Bo, 1991). The material was immersed in 0.5 wt% aqueous potassium permanganate solution (Shanghai Second Chemicals Company, China) for 1 h and washed with distilled water. The washed chitin was immersed in 1 wt% aqueous oxalic acid solution (Shanghai Fourth Chemicals Company, China) at 30 °C for 20 min. The resulting product was washed, dried and ground. LiCl and DMAc were from Shanghai Second and Third Chemicals Companies (China), respectively. All the reagents used in this work were analytical grade.

LiCl was heated to 160 °C to remove its water of crystallization completely. One part of dried LiCl was added to 20 parts of DMAc (by mass) to prepare LiCl,DMAc solvent system. Then known amounts of chitin were added to the solvent system at ambient temperature (20 °C) to produce the 1, 2 and 3 wt% chitin/LiCl,DMAc solutions.

The steady and dynamic rheological properties of the chitin solutions were measured on an advanced rheometric expansion system (ARES, Rheometric Scientific Inc., New Jersey, USA). The testing configuration was concentric cylinders. Steady measurements were carried out at 20 °C.

## 3. Results and discussion

Fig. 1 shows the curves of apparent viscosity ($\eta_a$) against shear rate ($\gamma$) for the chitin/LiCl,DMAc solutions. All the solutions containing different concentrations of chitin were non-Newtonian fluids, showing a viscosity that decreased with shear rate. Unlike chitin/DCA solutions in which the viscosity increases with chitin concentration (Chen et al., 2002), the 2 wt% chitin/LiCl,DMAc solution had lower viscosity than the 1 wt% chitin/LiCl,DMAc solution. The transition from the isotropic to the nematic state is marked by a decrease in the apparent viscosity as found by Hermans (1962). This is reasonable because molecules can slide past each other more readily in the nematic state than in the isotropic state (DuPré, Samulsk, & Tobolsky, 1971; Jin & Hua, 1999; Larson, 1999). Therefore, the decrease in the apparent viscosity in this work initially suggested that the 2 wt% chitin/LiCl,DMAc solution formed lyotropic liquid crystals, in which an ordered structure had been established.

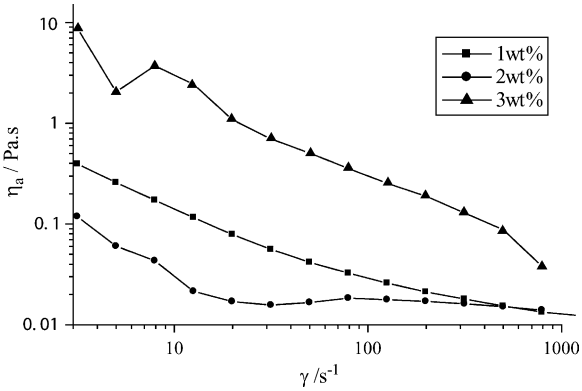

Fig. 1. Apparent viscosity $\eta_a$ vs. shear rate $\gamma$ curves for the chitin/LiCl,DMAc solutions with different concentrations.

The appearance and microstructure observed support this conclusion. The 2 and 3 wt% chitin/LiCl,DMAc solutions were light yellow, glittering and transparent, while the 1 wt% chitin/LiCl,DMAc solution did not have such an appearance but looked like common organic solutions. Under an optical microscope with cross polars (Leica-DMLP, Leica Microsystems AG, Germany) the 1 wt% chitin/LiCl, DMAc solution was dark and the other two had bright points, shinning areas and colourful stripes. As only anisotropic phases give images under the polarized optical microscope, it is reasonable to conclude from these observations and the decreased viscosity that both the 2 and 3 wt% chitin/LiCl,DMAc solutions formed lyotropic liquid crystals.

It is not abnormal to obtain liquid crystals from chitin due to its rigid benzene-ring backbone and rod-like morphology (Nge, Hori, Takemura, & Ono, 2003); the rigid polymers in suitable solvents can give rise to mesophases because they behave as rigid rods (Barnes, Hutton, & Walters, 1989; De Gennes & Prost, 1993; DuPré et al., 1971). Dong and Wang (1999) claimed that chitin/DCA solutions formed cholesteric liquid crystals. Nge et al. showed that pre-formed chitin crystallites transformed to chiral nematic (cholesteric) liquid crystals after suspending in acrylic acid. Li, Revol, and Marchessault (1996) also speculated from rheological testing that aqueous suspensions of pre-formed chitin crystallites appeared as chiral nematic liquid crystals and they turned to nematic phases under shear forces. With regard to molecular structure, nematic and cholesteric liquid crystals appear as two subclasses of the same family to some extent (De Gennes & Prost). According to the decreased apparent viscosity, the 2 wt% chitin/LiCl,DMAc solution formed nematic liquid crystals under shear forces (DuPré et al.; Larson, 1999). The ‘critical concentration’ of transferring a common solution of chitin/LiCl,DMAc is thus between 1 and 2 wt%.

The viscosity of the 3 wt% chitin/LiCl,DMAc solution was greater than that of the 2 wt% chitin/LiCl,DMAc solution. This can be explained by the co-existence of isotropic and anisotropic phases in the lyotropic liquid crystals (He & Chen, 1990). Once the concentration of a solution exceeds the ‘critical concentration’ as defined previously, the proportion of anisotropic phases in the solution increases with concentration until the solution becomes uniformly anisotropic. Correspondingly, the viscosity of this solution is reduced to its lowest value. After that, the viscosity increases rapidly again with concentration due to the formation of isotropic phases. Therefore, the relatively high viscosity in the 3 wt% chitin/LiCl,DMAc solution can be attributed to its higher proportion of isotropic phases compared to that in the 2 wt% chitin/LiCl,DMAc solution. However, it is not precluded that the types of the liquid crystal may change with the increasing concentration of chitin solutions (DuPré et al., 1971).

When the shear rate was relatively low, i.e. $\gamma < 12\ \mathrm{s}^{-1}$, the viscosities of the 2 and 3 wt% chitin/LiCl,DMAc solutions decreased more rapidly than that of the 1 wt% chitin/LiCl,DMAc solution, implying that the flowing units in the liquid crystals are oriented more easily. When the shear rate was increased, the viscosity was a function of the concentration, i.e. all the flowing units in both liquid crystals and the common polymer solution were oriented and hence there was no difference between them under high shear rates (He & Chen, 1990).

The structure viscosity index $\Delta\eta_a$ is defined as follows:

$$\Delta\eta_a = -(\mathrm{dlg}\ \eta_a/\mathrm{d}\gamma^{1/2}) \times 10^2$$

It can be used to characterize the structuralization of a spinning solution (Dong, 1981). A small $\Delta\eta_a$ implies low structuralization. It has been proved that the lower structuralization of a spinning solution, the better spinnability and fibre quality are achieved. Fig. 2 shows the curves of lg $\eta_a$ vs. $\gamma^{1/2}$ for the chitin solutions. Their slopes indicate that the 2 wt% chitin/LiCl, DMAc liquid crystals had the lowest $\Delta\eta_a$, suggesting the better spinnability and fibre quality. In contrast, the 3 wt% chitin/LiCl,DMAc liquid crystals had the worst spinnability having the highest viscosity among the three solutions.

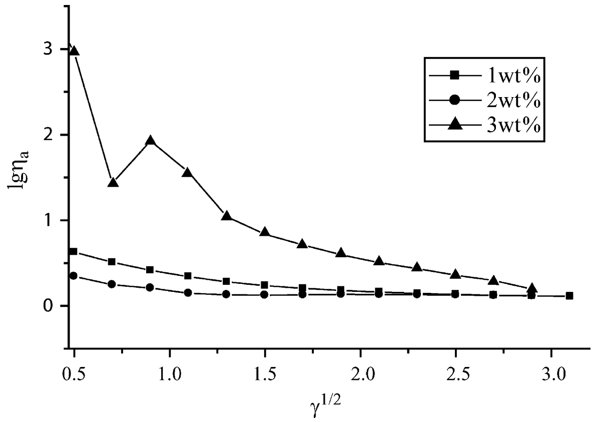

Fig. 2. Logarithmic apparent viscosity lg $\eta_a$ vs. square root shear rate $\gamma^{1/2}$ for the chitin/LiCl, DMAc solutions with different concentrations.

Dynamic rheological testing was conducted on the 3 wt% chitin/LiCl,DMAc solution to verify the formation of liquid crystals and to study the rheological properties more comprehensively. The linear viscoelastic zone was firstly investigated with frequency $\omega$ set at 10 rad $\mathrm{s}^{-1}$. Fig. 3 shows the curves of storage modulus ($G'$) and loss modulus ($G''$) against strain ($\varepsilon$). $G'$, equivalent to the first normal stress difference at steady state, was negative at 30 and 60 °C. This again implies that the 3 wt% chitin/LiCl,DMAc solution was a lyotropic liquid crystal, because negative first normal stress difference is one of the unusual rheological properties shown by some liquid crystals (Barnes et al., 1989; Larson, 1999; Wu & Wu, 1994). Larson attributed this negative value to a consequence of the frustration of tumbling that occurs when shearing is strong enough to distort the molecular order parameter. $G'$ also reflects the capability of storing energy during deformation and releasing it on unloading (Young & Lovell, 1991). For common polymer solutions, increasing temperature

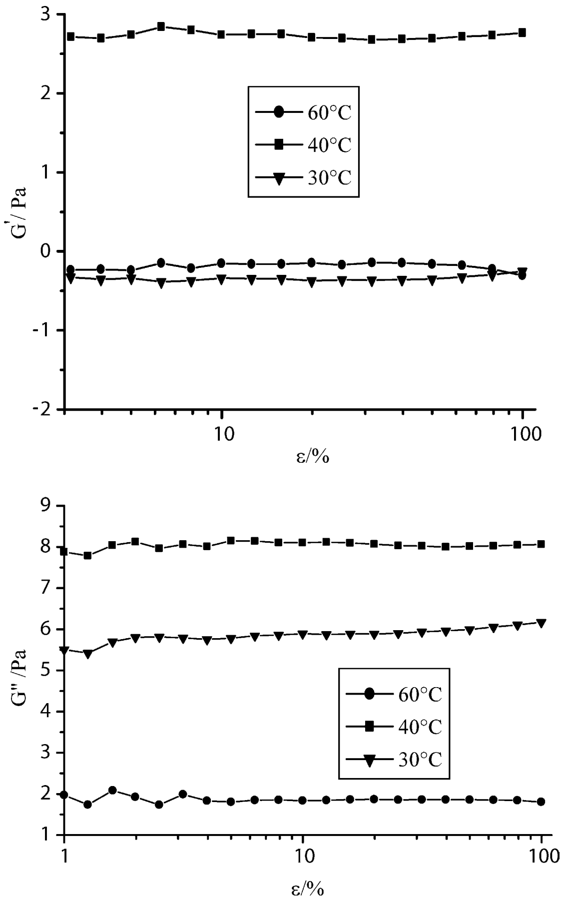

Fig. 3. Storage modulus $G'$ and loss modulus $G''$ vs. strain $\varepsilon$ for the 3 wt% chitin/LiCl,DMAc solution measured at different temperatures.

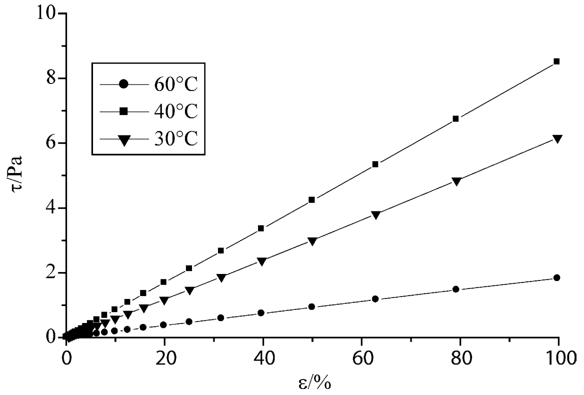

Fig. 4. Shear stress $\tau$ vs. shear strain $\varepsilon$ for the 3 wt% chitin/LiCl,DMAc solution measured at different temperatures.

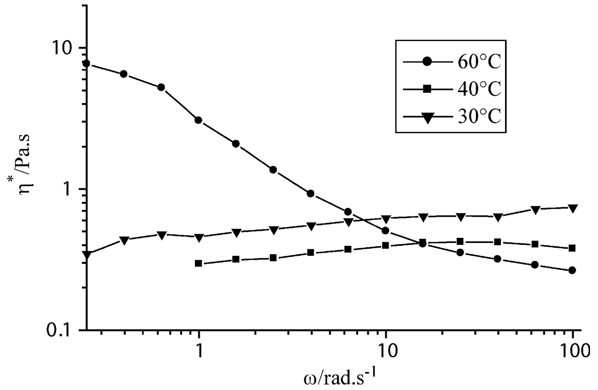

Fig. 5. Complex viscosity $\eta^*$ vs. frequency $\omega$ for the 3 wt% chitin/LiCl,DMAc solution measured at different temperatures.

promotes a polymer fluid to relax and decreases the elasticity by reducing its elastic storage energy when it flows out of spinning orifices (Dong, 1981). However, $G'$ for the 3 wt% chitin/LiCl,DMAc solution was changed in a different way by increasing temperature, again suggesting the existence of liquid crystals. It is important to find out an appropriate temperature for spinning fibres from liquid crystals.

Similarly $G''$ had the greatest value at 40 °C, supporting the existing conjecture that liquid crystals behave differently from common polymer solutions during rheological testing (He & Chen, 1990). The dynamic viscosity $\eta'$ reflecting the viscosity of a non-Newtonian fluid, can be deduced from $G''$ ($\eta' = G''/\omega$, where frequency $\omega = 10$ rad s$^{-1}$).

Fig. 4 shows the shear stress $\tau$–shear strain $\varepsilon$ curves for the 3 wt% chitin/LiCl,DMAc liquid crystals measured at different temperatures. All the three curves are linear, showing that the applied shear stress increases with shear strain. This also suggests that the yield stress has not been reached within the measurement range and the liquid crystals are in their linear viscoelastic zone. Thus when $\varepsilon < 100\%$, the deformation of the liquid crystals caused by the external shear stress can spring back to the original status. Under the same deformation, the stress at 40 °C was highest compared to that at other two temperatures, implying that the highest stress is required to overcome the resistance force during flowing and orientation. The change of the curve $\tau$ vs. $\varepsilon$ with temperature is again different from that for common polymer solutions in that the slope of the curve often decreases with temperature monotonically in the latter (He & Chen, 1990). The linear relationship between $\tau$ and $\varepsilon$ suggests that these curves follow Hooke's law which can be presented as modulus $G = \tau/\varepsilon$. In the present work, $G$ refers to complex modulus $G^*$. Thus the liquid crystals at 40 °C had the highest complex modulus, suggesting the largest shear modulus (Young & Lovell, 1991).

The frequency scanning was carried out with the strain set at 10%, a value within the linear viscoelastic zone. Fig. 5 shows the curves of complex viscosity $\eta^*$ against frequency $\omega$. $\eta^*$ is a combination of two parts, contributed by the viscous component $\eta'$ and the elastic component $\eta''$. The curves are nearly horizontal but when the temperature was increased to 60 °C, the relationship presents a negative slope. This is probably because some of the anisotropic phases in the solution have turned to isotropic phases at this temperature.

According to the Cox–Merz rule (1958), there is a relationship between complex viscosity $\eta^*$ ($\omega$) measured dynamically and $\eta_a(\gamma)$ measured in steady flow wherein $\omega$ is equal to $\gamma$ such that:

$$\eta^*(\omega) = \eta_a(\gamma)$$

Through this relationship, the dynamic curves can be considered as corresponding to the steady curves although it has been shown that the equation is not always valid (Li, Jarvela, & Jarvel, 1997; Twardow & Dennin, 2003). Within the measurement range, the liquid crystals at 30 and 40 °C were in the first Newtonian zone; however, those at 60 °C behaved as shear thinning, suggesting its inferior processing properties (Nelson, 1983). Therefore, a temperature ≥60 °C is not recommended as a spinning temperature for the 3 wt% chitin/LiCl,DMAc solution.

## 4. Conclusions

The steady and dynamic rheological properties of chitin solutions have been studied in order to guide spinning conditions. The 2 wt% chitin/LiCl,DMAc solution formed lyotropic liquid crystals as determined by its decreased apparent viscosity in contrast to the 1 wt% chitin/LiCl, DMAc solution. This is a well-known mark for the transition of isotropic solutions to anisotropic nematic liquid crystals. Observations from the appearances and polarized optical microscope supported this conclusion. The 3 wt% chitin/LiCl,DMAc solution was also a lyotropic liquid crystal as deduced from the appearance, microscope observation, negative first normal stress differences, and abnormal changing status with temperature.

Apart from lower apparent viscosity, the 2 wt% chitin/LiCl,DMAc liquid crystals had higher orientation at the zone of low shear rates, and less structuralization as compared with the 1 wt% chitin/LiCl,DMAc common solution. This indicates that the former had better spinnability and would give higher quality of fibre after spinning. The existence of liquid crystals solves the problems associated with higher viscosity and more structuralization that usually accompany common polymer solutions. Dynamic rheological testing on the 3 wt% chitin/LiCl,DMAc solution shows that increasing temperature did not always decrease the viscosity and elasticity, therefore selecting a spinning temperature for lyotropic liquid crystals needs additional caution. For the 3 wt% chitin/LiCl,DMAc liquid crystals, a temperature below 60 °C should be considered for spinning.

## References

Austin, P. R. (1977). *Chitin solution*. US patent 4,059,457.

Austin, P. R. (1984). Chitin solution. In J. P. Zikakis (Ed.), *Chitin, chitosan and related enzymes* (pp. 227–231). Orlando: Academic Press.

Barnes, H. A., Hutton, J. F., & Walters, K. (1989). *An introduction to rheology*. Amsterdam: Elsevier (pp. 13, 56, 105).

Chen, B. Q., Sun, K., Fan, Y. Z., & Zhang, K. B. (2002). Initial rheological studies on chitin solutions. *Journal of Functional Polymers*, *15*(3), 311–314.

Cho, Y. W., Cho, Y. N., Chung, S. H., Yoo, G., & Ko, S. W. (1999). Water-soluble chitin as a wound healing accelerator. *Biomaterials*, *20*(22), 2139–2145.

Cox, W. P., & Merz, E. H. (1958). Correlation of dynamic and steady follow viscosities. *Journal of Polymer Science*, *28*, 619–622.

De Gennes, P. G., & Prost, J. (1993). *The physics of liquid crystals* (2nd ed.). New York: Oxford University Press (pp. 14–18).

Dong, J. Z. (1981). *The processing of synthetic fibres*. Beijing: Textiles Industry Press.

Dong, Y. M., & Wang, J. W. (1999). Studies on chitin lyotropic liquid crystals. *Acta Polymerica Sinica*, *4*, 431–434.

DuPré, D. B., Samulski, E. T., & Tobolsky, A. V. (1971). The mesomorphic state: Liquid and plastic crystals. In A. V. Tobolsky, & H. F. Mark (Eds.), *Polymer science and materials* (pp. 123–160). New York: Wiley.

He, M. J., & Chen, W. X. (1990). *Polymer physics*. Shanghai: Fudan University Press.

Hermans, J., Jr. (1962). viscosity of concentrated solutions of rigid rodlike molecules. *Journal of Colloid Science*, *17*, 638–648.

Hirano, S., Zhang, M., Chung, B. G., & Kim, S. K. (2000). The N-acylation of chitosan fibre and the N-deacetylation of chitin fibre and chitin-cellulose blended fibre at a solid state. *Carbohydrate Polymers*, *41*(2), 175–179.

Jin, R. G., & Hua, Y. Q. (1999). *Polymer physics*. Beijing: Chemistry Industry Press (pp. 47–48).

Larson, R. G. (1999). *The structure and rheology of complex fluids*. New York: Oxford University Press (pp. 503–547).

Li, J., Revol, J-F., & Marchessault, R. H. (1996). Rheological properties of aqueous suspensions of chitin crystallites. *Journal of Colloid and Interface Science*, *183*, 365–373.

Li, S., Jarvela, P. K., & Jarvela, P. A. (1997). A comparison between apparent viscosity and dynamic complex viscosity for polypropylene/maleated polypropylene blends. *Polymer Engineering and Science*, *37*(1), 18–23.

Liu, S. Y., & Wu, Q. J. (1994). Recent development and foreground of chitin and chitosan fibres in medical fields. *Industry Textiles*, *12*, 10–12.

Lu, F. Q., & Cao, Z. S. (1993). Effects of preparation on the properties of deacetylated chitin. *Chemistry Society*, *3*, 138–140.

Matsuyama, H., Kitamura, Y., & Naramura, Y. (1999). Diffusive permeability of ionic solutes in charged chitosan membrane. *Journal of Applied Polymer Science*, *72*(3), 397–404.

Muzzarelli, R. A. A. (1977). *Chitin*. Oxford: Pergamon Press.

Muzzarelli, R. A. A. (1993). Biochemical significance of exogenous chitins and chitosans in animal patients. *Carbohydrate Polymers*, *20*(1), 7–16.

Nelson, L. E. (1983). *Polymer rheology*. Beijing: Science Press.

Nge, T. T., Hori, N., Takemura, A., & Ono, H. (2003). Phase behavior of liquid crystalline chitin/acrylic acid liquid mixture. *Langmuir*, *19*, 1390–1395.

Okamoto, Y., Kawakami, K., Miyatake, K., Morimoto, M., Shigemasa, Y., & Minami, S. (2002). Analgesic effects of chitin and chitosan. *Carbohydrate Polymers*, *49*(3), 249–252.

Onishi, H., Nagai, T., & Machida, Y. (1997). Applications of chitin, chitosan, and their derivatives to drug carriers for microparticulated or conjugated drug delivery systems. In M. F. A. Goosen (Ed.), *Application of chitin and chitosan* (pp. 407–409). Cancaster, PA: Technomic Pub. Co.

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

Shierrdon, R. P. (1989). *Polymeric composites*. Beijing: Light Industry Press.

Striegel, A. M. (1997). Theory and applications of DMAC/LICL in the analysis of polysaccharides. *Carbohydrate Polymers*, *34*, 267–274.

Su, C.-H., Sun, C.-S., Juan, S. W., Ho, H. O., Hu, C. H., & Sheu, M. T. (1999). Development of fungal mycelia as skin substitutes: Effects on wound healing and fibroblast. *Biomaterials*, *20*(1), 61–68.

Tokura, S., Baba, S., Uraki, Y., Miura, Y., Nishi, N., & Hasegawa, O. (1990). Carboxymethyl-chitin as a drug carrier of sustained release. *Carbohydrate Polymers*, *13*(3), 273–281.

Twardow, M., & Dennin, M. (2003). Comparison of steady-state shear viscosity and complex shear modulus in langmuir monolayers. *Langmuir*, *19*, 3542–3544.

Wang, W., Qin, W., & Bo, S. Q. (1991). Influence of the degree of deacetylation of Mark-Houwink equation parameters. *Makromolecu-lare Chemie-Rapid Communications*, *12*(9), 559–561.

Wu, Q. Y., & Wu, J. A. (1994). *Introduction to polymer rheology*. Beijing: Chemistry Press.

Wu, Z. X., & Wu, G. M. (1997). Chemical reactions of chitin and their applications. *Chemical Fibres in Guangdong*, *12*(4), 13–16.

Young, R. J., & Lovell, P. A. (1991). *Introduction to polymers* (2nd ed.). London: Chapman & Hall (pp. 334–335).