Maejo Int. J. Sci. Technol. **2010**, *4*(02), 210-220

Maejo International
Journal of Science and Technology

ISSN 1905-7873
Available online at www.mijst.mju.ac.th

Short Review

Rheological study of chitosan and its blends: An overview

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Received: 11 September 2009 / Accepted: 31 May 2010 / Published: 3 June 2010

Abstract: Chitosan, a modified natural carbohydrate polymer derived from carapaces of crabs and shrimps, has received a great deal of attention for its applications in diverse fields owing to its biodegradability, biocompatibility, non-toxicity and anti-bacterial property. The wide-ranging applications involve a broad spectrum of characterisation techniques and rheology represents one technique of growing importance in this field. This paper is an attempt to review the latest development in the rheology of chitosan, either on its own or associated with other materials, including the parameters that strongly influence its rheological behaviour such as concentration, pH and temperature.

Keywords: chitosan, chitosan blends, chitosan gels, cross-linked chitosan, rheology

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Introduction

Chitosan, or (1 → 4)-2-amino-2–deoxy-β-D–glucan (Figure 1), is the deacetylated derivative of chitin [1-2], the most abundant natural polymer on earth after cellulose [3-5] and obtained from crustaceans [6-7] such as shrimps, squids and crabs. Chitosan is readily prepared from chitin [8-9].

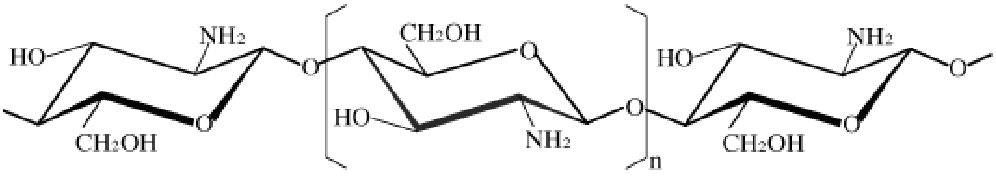


Figure 1. Chemical structure of chitosan

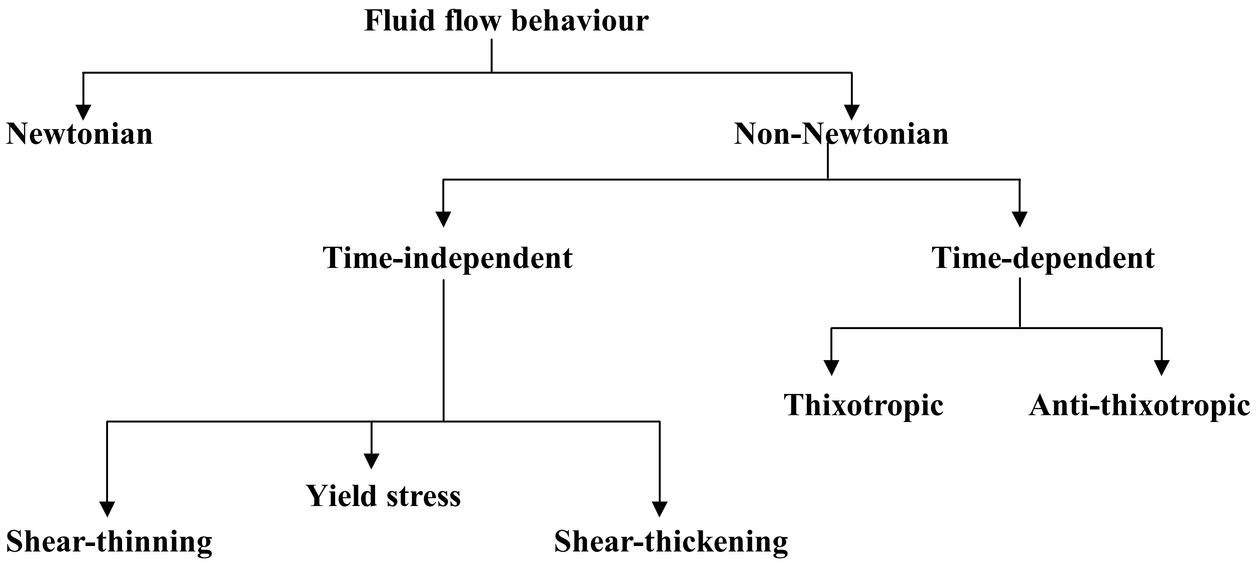
Chitosan can be dissolved in aqueous solutions of organic acids such as formic acid and acetic acid at a pH below 6.2 due to protonation of the free amino groups present in its molecular structure [10]. Chitosan hardly dissolves in pure acetic acid. In general, the properties of chitosan solutions depend on several parameters including degree of deacetylation [11], pH [12-13], ionic strength [12], concentration [14], temperature [15], acid concentration [16], type of acid [17], and distribution of the acetyl groups along the chain [18-19]. For example, Matsumoto et al. [11] demonstrated that the solutions of chitosan with 62% and 96% degree of deacetylation (DD) are homogeneous while that with 76% DD is heterogeneous. Chen et al. [12] reported that the viscosity of chitosan solutions is significantly affected by ionic strength, pH and counter ions. Tsaih and Chen [13] revealed that viscosities of solutions of chitosan with the same molecular weight decrease with increasing pH, while viscosities of solutions of chitosan with the same pH increase with increasing molecular weight. A chitosan solution stored at 4^{o}C is found to be relatively stable from a viscosity point of view [20].

Similar to most natural polymers, chitosan has an amphiphilic character which can influence its physical properties in solutions and solid states. This is attributed to the presence of the hydrophilic amino groups and the hydrophobic acetamido groups in its molecular structure. Unlike most polysaccharides, chitosan can carry strong positive charges because it possesses a great number of amino groups, thus endowing this polymer with many useful properties such as the capacity to form composite materials when blended with other polymers [21].

Chitosan shows great promise for a wide variety of uses. Unique properties such as biodegradability [22], biocompatibility [23-24], non-toxicity [25] and anti-bacterial activity [26] are the main driving forces pushing studies on new applications of this polymer. Chitosan has already been used in many fields including wastewater treatment, medicine, food and cosmetics [27-33]. Due to the importance of rheology in various fields of science and technology, this short review tries to present the recent (approximately from 1980 to the present) rheological studies involved with chitosan as well as its blends, although such studies are quite limited in the literature.

Rheological Properties

Rheology is defined as the science of the deformation and flow of matter [34-36]. It investigates the response of materials to an applied stress or strain [37-38]. Rheological properties describe flow characteristics and textural behaviour of substances. The success of a wide range of commercial products and industrial processes depends on meeting specific flow requirements. Rheological behaviour can be generally divided into two types [39]: elastic behaviour, where the material restores its original shape when the external force is removed, and viscous or plastic behaviour (such as in ideal Newtonian liquids), where deformation ceases and the material does not regain its original shape when the applied force is removed. The fluid flow behaviour is summarised in Scheme 1 and Figure 2.



Scheme 1. Fluid flow behaviour

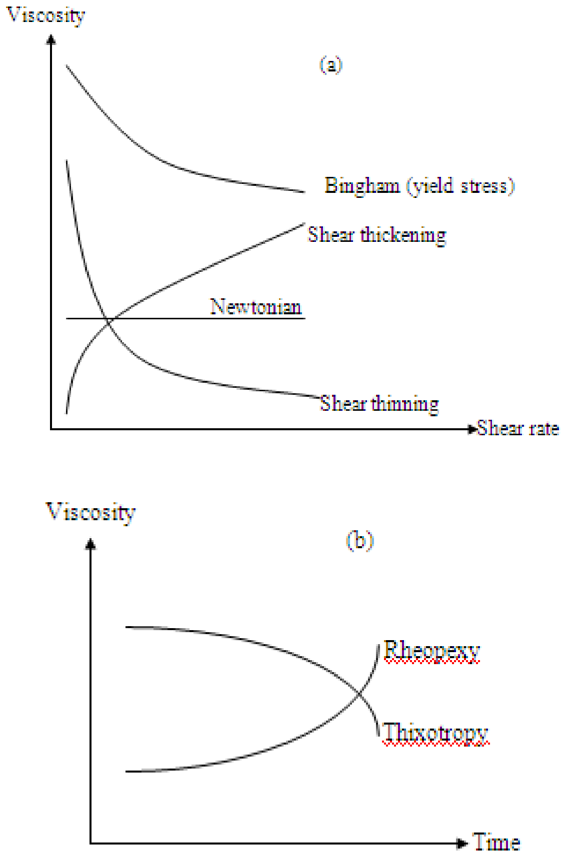


Figure 2. The relationship between (a) apparent viscosity and shear rate for time-independent fluids and (b) apparent viscosity and time for time-dependent fluids

Rheology of Pure Chitosan Solutions and Gels

The rheological behaviour of chitosan depends on the concentration of its solution [40-48]. Kienzle-Sterzer et al. [42] found that the viscosity of concentrated chitosan solutions increases with increasing chitosan concentration and that a shear thinning behaviour is observed at the polymer concentrations above 0.50 g/dL. They also reported the independence and dependence of the zero shear viscosity on the ionic strength and pH of the media respectively.

Wang and Xu [43] reported that the non-Newtonian behaviour of chitosan solutions increases with increasing DD, which can be attributed to the chain-expanding structure and consequent increase in entanglement. Mucha [44] also reported an increase in the shear stress and viscosity of chitosan solutions with increasing chitosan concentration also due to the increase in entanglement among the macromolecular chains.

The rheology of two aqueous systems of chitosan—unmodified chitosan and hydrophobically-modified chitosan—was studied by Nyström et al [46]. Their results revealed that the linear and non-linear viscoelasticity are affected by several factors such as pH, temperature, amount of surfactant, and polymer concentration. The HM-chitosan was found to be more influenced by these factors. In addition, the shear thinning behaviour is more pronounced at higher shear rates for both systems. Hwang and Shin [47] noted that the shear rate dependence of viscosity is more remarkable at higher chitosan concentrations.

Martinez et al. [48] studied the influence of some parameters such as temperature, acid type and addition of salt, on the steady-shear rheology of concentrated chitosan solutions. Viscosity and normal stress were observed to decrease with increasing temperature and decreasing chitosan concentration. In addition, chitosan in hydrochloric acid solutions exhibits lower steady-shear viscosity and normal stress than in other acid solutions. Addition of salt was found to be the most effective parameter on the rheology of chitosan solutions, i.e. the presence of salt decreases viscosity due to the interaction between charged chains and small ions in solution.

Bodek [49] studied the rheological properties of microcrystalline chitosan hydrogels prepared by adding a methylcellulose hydrogel to aqueous chitosan dispersions. It was found that, depending on the kind and content of the pharmaceutical substances as well as the interactions between the polymer and the pharmaceutical substances, a pseudo-plastic system can be observed. Anchisi et al. [50] showed that rheological properties of chitosan dispersions are affected by the molecular weight and that all chitosan dispersions show a pseudo-plastic and shear thinning behaviour. It was also found that the presence of glycols leads to decrease in the apparent viscosity compared to that in the corresponding base dispersions.

The formation of chitosan hydrogels in an acetic acid-water-propanediol medium was reported by Montembaulta et al [51]. The gelation at different polymer concentrations, the degree of acetylation (DA) of chitosan, and the composition of the initial solvent were studied by rheometry. It was found that the optimal gelation conditions for cartilage regeneration application are: DA = 40%, ratio of water/alcohol (solvent) = 1:1, and polymer concentration = 1.5%.

The production of pH-induced monolithic hydrogels through uniform neutralisation of slightly acidic chitosan solutions with ammonia generated from enzymatic hydrolysis of urea was analysed via rheology and reported by Chenite et al [52]. A decrease in gelation time with increase in temperature from 15 to 45°C was pronounced to be a result of the synergistic influence of increased reactant diffusion and increased urease activity. It was also observed that gelation is accelerated as the urea concentration increases up to a certain limit and then a slow decrease of the gelation kinetics was noticed. This study indicates the possibility of using the auto-gelling solutions of chitosan as injectable gels for tissue engineering and drug delivery.

Fernandez et al. [53] reported the rheology of chitosan gels with different (low and medium) molecular weights. Non-Newtonian flow independent of time was observed for the two gels, with pseudo-plastic behaviour for low-molecular-weight gel and plastic behaviour for medium-molecular-weight gel. Mironov et al. [54] reported a decrease in the dynamic viscosity of chitosan solutions in acetic acid during storage due to polymer degradation.

The effect of some parameters such as temperature, concentration, shearing time and storage time on the rheological properties (apparent viscosity and shear stress) of chitosan dissolved in acetic acid was reported by Elhefian et al [55]. The shear-thinning behaviour, which is more pronounced at a lower temperature, was observed for chitosan solutions at all temperatures and concentrations studied. When shearing time was studied, no significant changes in the dynamic viscosity and shear stress of chitosan solutions were observed. In addition, when the period of storage was extended to 3 months, an increase in viscosity was recorded at a constant shear rate, after which a drop in the viscosity was observed.

Rheology of Cross-Linked Chitosan Solutions

Argüelles-Monal et al. [56] reported an apparent yield stress at very low frequencies for chitosan in acetic acid solution and a cross-linking reaction between chitosan and glutaraldehyde, in which the chemical cross-linkage between the aldehydic groups of glutaraldehyde and the amino groups of chitosan was supposed to take place leading to the weak self-associated network of chitosan being gradually replaced by a permanent covalent network. A strong permanent gel was reported to form at higher cross-linking levels.

Moura et al. [57] reported the rheology of solutions of chitosan cross-linked with a natural cross-linker, genipin, at various concentrations. Stronger elastic gels of the cross-linked solutions were obtained under physiological conditions compared to those of the pure component. They also reported that the value of the gelation time obtained from the crossover of G'' (loss modulus) and G' (storage modulus) and that recorded by the Winter–Chambon criterion were in excellent agreement.

Rheology of Solutions and Gels of Chitosan Blends

The rheological characteristics of solutions of chitosan and polyoxyethylene of various molecular weights were reported by Nikolova et al [58]. Pseudo-plastic non-Newtonian behaviour was observed for each of the pure polymer solutions as well as those of their mixtures. It was assumed that the rheological behaviour of the chitosan/polyoxyethylene mixtures is determined by chitosan macromolecules. Khalid et al. [59] reported the rheological properties of a semi-interpenetrating chitosan–polyethylene oxide network. Their results showed that the elastic properties increase with the semi-interpenetration due to the presence of the polyethylene oxide physical network.

Jiang et al. [60] investigated the phase transition behaviour of water within the chitosan/polyacrylate hydrogels with variation in temperature and frequency using oscillatory shear rheology. The results indicated that the water phase transition which occurs with a decrease in temperature has a significant influence on all the viscoelastic properties measured (shear storage modulus, shear loss modulus and shear loss tangent). The changes of the viscoelastic properties were found to be related to the mobility of water within the gels.

The preparation of thermogelling chitosan/glycerol-phosphate solutions by neutralising highly deacetylated chitosan solutions up to physicological pH (~ 7.2) with β-glycerol phosphate was reported by Chenite et al [61]. Rheological measurements demonstrated that the hydrogel formation by subsequent heating of these solutions is quickly obtained. The study also showed the pH sensitivity of the sol/gel transition temperature and the temperature dependence of the gelling time. Based upon the observations obtained, multiple interactions between chitosan, glycerol phosphate and water were suggested for the molecular mechanism of the gelation.

Salomé Machado et al. [62] reported the preparation and characterisation of collagen/chitosan blends by rheological studies. A decrease of storage modulus, viscous loss modulus and apparent viscosity (as a function of frequency) was observed with the addition of chitosan to collagen. It was also found that collagen/chitosan blends present a more fluid-like viscoelastic behaviour than solid-like one.

The rheological properties of kaolin/chitosan aqueous dispersions were characterised by Bezerril et al [63]. The kaolin/chitosan dispersions show a pseudo-plastic behaviour which increases at lower shear rate. The increase in pseudo-plasticity was related to a higher occurrence of particle-polymer-particle interactions stemming from the adsorption of chitosan macromolecules on the surface of kaolin particles. The rheological behaviour of these dispersions could not be described by a simple power law.

The rheological properties of chitosan/xanthan hydrogels were studied by Martı´nez-Ruvalcaba et al. [64]. Their results showed that chitosan/xanthan hydrogels behave like weak gels. An almost linear increase in the shear modulus was observed with frequency in the range between 0.1-65 s^{-1}. It was also found that other factors such as hydrogel concentration and nature of dispersion have a significant role in the final structure and the final properties of the hydrogels. The viscoelastic properties of chitosan/PVA hydrogel were investigated rheologically by Tang et al [65]. Their results indicated a good mechanical strength of the gel.

Madrigal-Carballo et al. [66] determined the rheological behaviour of lecithin/chitosan vesicles by means of shear stress against shear rate measurements. The results showed that chitosan can promote the transition of planar sheets into closed structures such as vesicles. It was also found that this system suggests a thixotropic behaviour. Chitosan solutions containing glycerol-2-phosphate were prepared and analysed by Kempe et al [67]. Their rheological properties were studied using oscillating rheology for characterising the micro-viscosity of the sol and gel systems. It was found that an amount of 6% glycerol-2-phosphate is necessary to induce gel formation and that neither the gelation process nor the chitosan/glycerol-2-phosphate proportion has an effect on the pH to a significant extent.

Wanchoo et al. [68] investigated the miscibility of chitosan blends with hydrophilic polymers: chitosan/polyvinyl alcohol, chitosan/polyvinylpyrrolidone and chitosan/polyethylene oxide. Rheological data showed that rheograms of all the blends lie between those of pure components over the entire compositional range, indicating that the miscibility of the blends may occur.

The rheology of chitosan/magnesium aluminum silicate (MAS) composite was reported by Khunawattanakul et al [69]. The addition of MAS to chitosan dispersions leads to an increase in viscosity and a change in flow type of chitosan from Newtonian to pseudo-plastic flow with thixotropic properties. It was suggested that the change in the flow behaviour is due to the electrostatic interaction between chitosan and MAS since they carry a positive and a negative charge respectively. Based on these findings, it was concluded that the chitosan–MAS composite dispersions can be applied as suspending and gelling agents in pharmaceutical products.

The rheological study of chitosan/gelatin composite was investigated by Wang et al [70]. Their results showed that the formation of a complex between chitosan and gelatin is mainly through hydrogen bonds and that there is a close relation between the interactions of these two polymers in solution and the mechanical properties of the films formed.

The preparation of chitosan ferrogels was reported by Herandez et al [71]. The method used was the simultaneous co-precipitation of Fe ions in alkali media and chitosan. The reinforcement of the chitosan ferrogels is achieved in the presence of magnetite nanoparticles, as evidenced by the increase in the viscoelastic modulus measured.

Elhefian et al. [72] studied the rheological properties of solutions of chitosan/agar blends with chitosan as the major component at temperatures from 40 to 55°C. A Newtonian behaviour was demonstrated at all temperatures studied for the blend proportions of 100/0, 90/10, 80/20 and 70/30. However, a shear-thinning behaviour was observed for the 60/40 and 50/50 proportions, which could be attributed to the formation of a good interaction between chitosan and agar. All the blend solutions were found to obey the Arrhenius equation. No significant difference in the apparent viscosity of any blend solution was observed at all shearing times applied with exception of the 50/50 blend where a decrease in the viscosity was observed with increasing shearing time. Different behaviours were observed for the blend solutions when the period of storage was extended to three weeks.

Conclusions

Owing to the importance of rheology in several fields and products inclucing chitosan, this brief review has attempted to describe the recent studies on the rheology of solutions of chitosan including some of its cross-linked derivatives and a variety of its blends. It is anticipated that rheology will be an indispensable tool for chitosan research in the future.

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