Short Communication

Effects of temperature, shearing time and rate of shear on the viscosity of chitosan/agar-blend solutions

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Abstract: In this study, a number of aqueous solutions of chitosan/agar blends (with chitosan as the major component) were prepared. The effects of temperature, shear rate and shearing time on the rheological property, i.e. the apparent viscosity, were investigated for the blend solutions. Results show that a non-Newtonian behaviour was pronounced at temperatures from 20°C to 50°C for all solutions and that a decrease in viscosity with increasing temperature was also observed. It was also found that all the blend solutions obeyed the Arrhenius equation to different degrees. In addition, shearing time independence was found to occur at a low shear rate only for pure chitosan solution. However, the shearing time independence slowly shifted to occur at higher shear rate with increasing agar content.

Introduction

Chitosan and agar are natural polymers that are much used in food, cosmetic, pharmaceutical and some other industries [1-5]. Chitosan is a polysaccharide formed by alkaline deacetylation of chitin, the second most abundant naturally occurring polysaccharide from crab and shrimp shells [6]. Agar, on the other hand, is a hydrocolloid extracted from seaweed and mainly consists of agarose and agaropectin [7]. One unique property of agar is that the gelation occurs at a temperature far below the gel's melting temperature, which leads to the formation of a rigid gel. These polymers are non-toxic, biodegradable, biocompatible and easily available.

Extensive studies on both chitosan and agar have been done in order to provide useful data for their applications. However, the work on both of them together, especially with respect to rheological properties, is very limited and thus, this forms the basis for studying them in the form of blends.

Earlier, we reported on the rheology of chitosan/agar-blend solutions at different proportions [8]. The study was conducted at temperatures ranging between 40-55°C with shearing times of 15, 30, 45, 60 and 75 seconds. However, the temperature range studied was small due to the gel formation of some blends below 40°C. The objective of this work is to study the effects of temperature, shearing time and rate of shear on the viscosity of chitosan/agar-blend solutions using smaller amounts of agar and a wider range of temperature for a better understanding of the flow behaviour of these blends.

Materials and Methods

Materials

Shrimp-source chitosan was purchased from a local company with a deacetylation percentage of 88.1% (defined by UV method [9]). This chitosan was acid soluble, white-coloured and flaky. Agar, powdery and light beige in colour, was purchased from Sigma (average molecular weight = 1.3 $\times 10^{4}$ g mol^{-1}). Acetic acid was purchased from Merck (Darmstadt, Germany). Ultra-pure water (Maxima Ultra Pure Water, Elga-Prima Corp., UK) with a resistivity greater than 18 MΩ/cm was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were used in all experiments.

Preparation of chitosan/agar-blend solutions

Chitosan, oven-dried to constant weight (5 g), was dispersed in 0.1 M acetic acid (500 mL) followed by stirring and heating at about 60°C overnight to form a 10 g L^{-1} chitosan solution, which was then filtered to remove dust and other traces of impurities. Air bubbles were eliminated by keeping the solution at room temperature for 2 hours. An agar solution was similarly prepared following the above procedure except 0.1 M acetic acid was replaced by preheated ultra-pure water. The solution was then stirred and kept at 80°C for 3 hours to ensure complete dissolution of agar and a very clear solution.

The chitosan/agar blends were prepared by adding the aqueous agar solution drop by drop to the chitosan solution, which was kept stirring on a magnetic stirrer at about 90°C, and then the mixture was stirred at a moderate speed for a certain time. The chitosan/agar-blend solutions thus prepared, with chitosan as the major component, had the blend ratio of 100/0 (pure chitosan), 90/10, 80/20, 70/30, 60/40 and 50/50.

Methods

The molecular weight of chitosan was about 5.5×10^{5} g mol^{-1} determined by gel permeation chromatography [10].

The viscosity of all solutions was determined by using a Brookfield digital viscometer, model DV-II + Pro, with an attached UL adapter. The temperature was maintained by using a circulating water bath. The viscosity was determined in a 16-mL of sample from 20°C to 50°C and shearing times were 20, 40, 60, 80 and 100 seconds. The shear rate was measured automatically by the instrument once set. The apparent viscosity values were reported in centipoise (cP) unit.

It is worth mentioning that it is necessary to use freshly prepared mixtures as any delay can make it difficult to measure the viscosity due to the formation of gel, especially for the mixtures containing higher than 20% agar.

Results and Discussion

Figure 1 shows the relation between viscosity and shear rate at different temperatures for solutions of pure chitosan and its blends with agar. Generally, two regions of flow profiles—low-shear and high-shear regions—can be identified. In low-shear region, the shear-rate-dependent viscosity decreased dramatically suggesting shear thinning behaviour (non-Newtonian behaviour). However, the shear-rate-dependent viscosity was found to be nearly independent of shear rate at high shear rates. Non-Newtonian materials are of significance in the pharmaceutical area since they are used to produce liquid and solid dispersions [11]. In addition, lower shear thinning and higher viscosity was observed when the concentration of agar was increased. Furthermore, the pure chitosan solution showed increasing shear thinning with increase in temperature. The viscosity range for this solution was 7-20 cP for shear rate ranging between 2-15 s^{-1}. As the proportion of agar increased, the solution became more viscous for each shear rate value, but showed the same trend with respect to temperature. The viscosity increased further with increase in amount of agar and tailed off at a slightly higher viscosity at the highest shear rate. As expected the last blend (50/50) with the highest agar content showed the highest viscosity values. The reason for this is most likely due to the gelling capacity of the agar. It is thought that improving the viscosity of the solution may improve the strength of the resulting thin film.

According to the Arrhenius equation, the viscosity values (η) obtained at a constant shear rate can be correlated with temperature:

$$\eta = A \cdot e^{-Ea/RT}$$

where A is a constant related to molecular motion, E_a is the activation energy for viscous flow at a constant shear rate, R is the gas constant and T is the absolute temperature in K.

Figure 2 presents the Arrhenius plots of the natural log of viscosity versus the inverse of temperature for various ratios of chitosan/agar-blend solutions. This graph shows a nearly linear relationship for all solutions. The values of the apparent activation energy (E_a), which were calculated from the slope, are shown in Table 1. Knowing the activation energy is important in deducing the sensitivity of a process towards temperature [12]; the higher the activation energy, the more sensitive the process is to temperature. The activation energy is also useful for signifying the minimum amount of energy required for the reactants to start a reaction [13]. The lower the activation energy, the faster the reaction will proceed. The lower values of E_a may indicate a good compatibility of the two polymers.
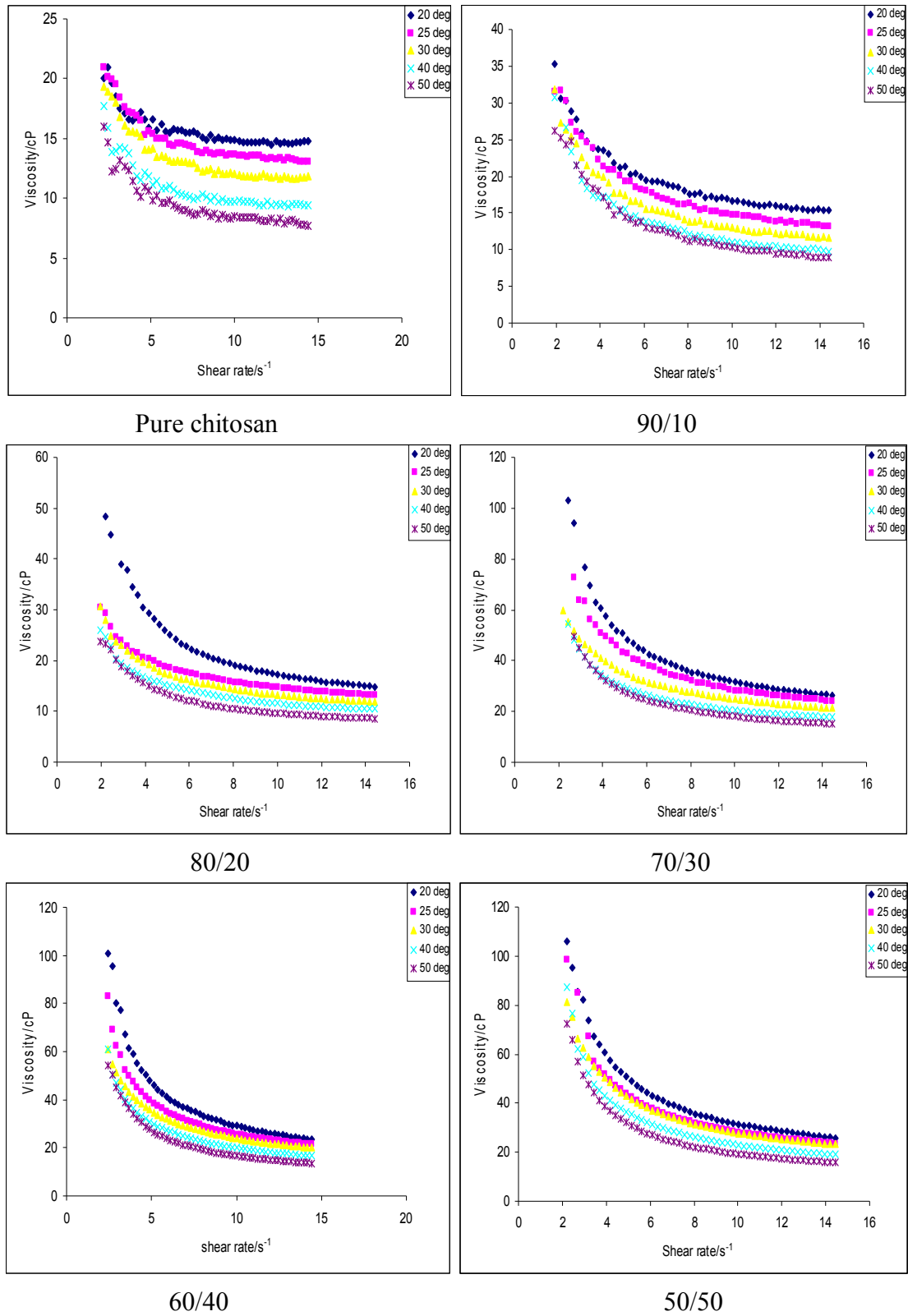
Figure 1. The influence of shear rate and temperature on the rheological curves of pure chitosan solution and its blends with agar at different proportions
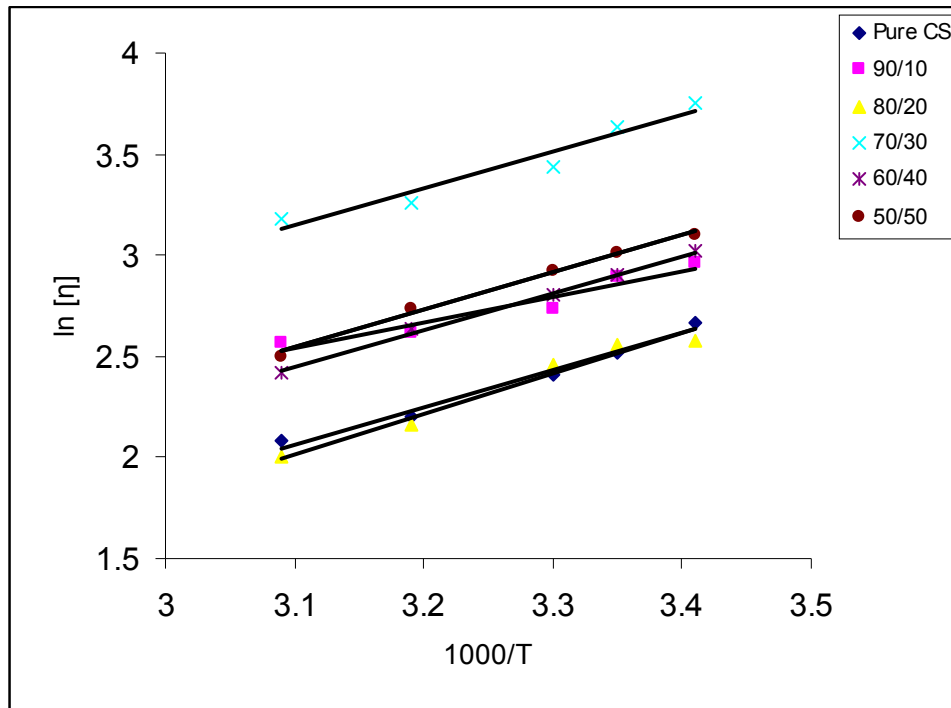
Figure 2. The relationship between apparent viscosity and temperature of chitosan/agar-blend solutions at a constant shear rate (6.15 s^{-1})

Table 1. The relationship between viscous flow activation energy and blend concentration

Chitosan/Agar	Viscous flow activation energy, E_a (kJ mol^{-1})
100/0	15.31
90/10	10.52
80/20	16.51
70/30	15.12
60/40	15.21
50/50	15.40

Figure 3 presents the effects of shear rate and shearing time on the rheological curves of pure chitosan solution and its blends with agar at room temperature. For pure chitosan solution at low shear rate, viscosity was independent of shearing time but becoming more dependent at higher shear rate. With added agar the opposite seemed to occur. At 10% agar, the viscosity became more dependent of shearing time at low shear rate and slightly less dependent of shearing time at higher shear rate. For the 80/20 blend, viscosity dependence on shearing time was almost the same for all shear rate values. For the 70/30 blend, clear independence of shearing time was observed at high shear rate values, and this is more pronounced with the 60/40 and 50/50 blends. In pure chitosan solution, shearing time independence occurred at low shear rate. The reason is most likely due to the absence of gelling property, which was present in the blend solutions, especially those with 30, 40 and 50% agar.
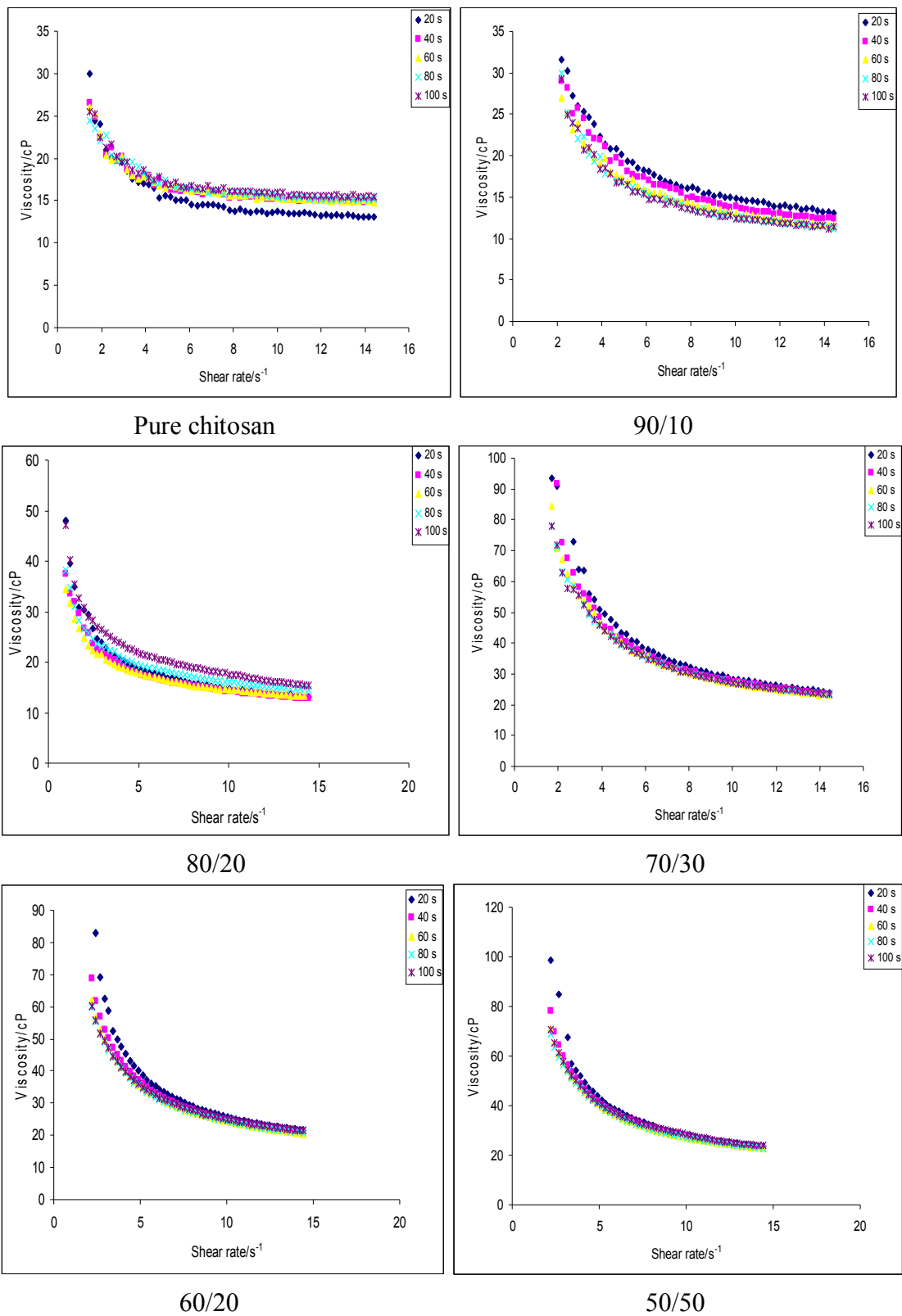
Figure 3. The influence of shear rate and shearing time on the rheological curves of pure chitosan and its blend solutions with agar at different proportions at room temperature

Conclusions

This study has shown that the viscosity of chitosan/agar-blend solutions increases significantly as the agar ratio is increased and that the temperature effect is the same for all blends, i.e. the overall viscosity decreases as the temperature increases. Also, a shear thinning behaviour was observed for all blend solutions at all temperatures studied. In addition, the relationship between the apparent viscosity and temperature can be described by the Arrhenius equation. Furthermore, shearing time independence occurs at low shear rate only for pure chitosan solution; for the blends, this phenomenon gradually shifts to higher shear rate as the agar content increases.

Acknowledgements

References

1. R. Armisen, "Worldwide use and importance of gracilaria", *J. Appl. Phycol.*, **1995**, *7*, 231-243.
2. Y. Freile-Pelegrín, T. Madera-Santana, D. Robledo, L. Veleva, P. Quintana and J. A. Azamar, "Degradation of agar films in a humid tropical climate: Thermal, mechanical, morphological and structural changes", *Polym. Degrad. Stab.*, **2006**, *92*, 244-252.
3. E. Khor and L. Y. Lim, "Implantable applications of chitin and chitosan", *Biomaterials*, **2003***, 24*, 2339-2349.
4. S. Yuan and T. J. Wei, "New contact lens based on chitosan/gelatin composites", *Bioact. Compat. Polym.*, **2004**, *19*, 467-479.
5. G. Crini, "Non-conventional low-cost adsorbents for dye removal: A review", *Bioresour. Technol.*, **2006***, 97*, 1061-1085.
6. H. I. Bolker, "Natural and Synthetic Polymer: An Introduction", Marcel Dekker, New York, **1974**, pp.106-109.
7. H. Moritaka, M. Takahashi and K. Kuboa, "Effects of cooling rate and sodium chloride on polysaccharide gelation", *Food Sci. Technol. Res.*, **2007**, *13*, 345-350.
8. E. A. El-hefian, M. M. Nasef, A. Yahaya and R. A. Khan, "Preparation and characterization of chitosan/agar blends", *J. Chil. Chem. Soc.***, 2010**, *55*, 130-136.
9. R. A. A. Muzzarelli and R. Rochetti, "Determination of the degree of acetylation of chitosans by first derivative ultraviolet spectrophotometry", *Carbohydr. Polym.*, **1985**, *5*, 461-472.
10. E. A. El-hefian, A. Yahaya and M. Misran, "Characterisation of chitosan solubilised in aqueous formic and acetic acids", *Maejo Int. J. Sci. Technol.*, **2009**, *3*, 415-425.
11. A. N. Martin, "Physical Pharmacy: Physical Chemistry Principles in the Pharmaceutical Science", Lea e Febiger, Philadelfia, **1993**, pp. 453-476.
12. M. Turhan and S. Gunasekaran, "Kinetics of in situ and in vitro gelatinization of hard and soft wheat starches during cooking in water", *J. Food Eng.*, **2002**, *52*, 1-7.
13. H. S. Fogler, "Elements of Chemical Reaction Engineering", Prentice-Hall, Upper Saddle River, NJ, **1999**, pp. 69-70.