

Characterization of Aqueous Solutions of Mixture of Chitosan and Agar

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Summary: The influence of temperature on pH and dynamic viscosity of pure chitosan and mixture of chitosan/agar (cs/ag) solutions was studied over a temperature range of 20°C to 50°C. It was found that the pH of chitosan/agar ratio of 60/40 is the highest affected solution by temperature while all the solutions showed similar effect by temperature in terms of viscosity at a constant shear rate. Results also showed that the temperature dependence of pure chitosan solution and chitosan/agar mixtures can be described using Arrhenius equation. Apparent activation energies were found to be 15.41, 16.52, 15.21 and 15.46 kJ mol⁻¹ for chitosan/agar proportions of 100/0, 80/20, 60/40 and 50/50 respectively. Relatively high activation energy at 50/50 composition can be attributed to the co-continuous morphology of the blend at the particular composition. The effect of the presence of agar in chitosan solutions on the viscosity as a function of shear rate was also examined at room temperature. Generally, results showed two regions of flow profiles; low shear rate and high shear rate regions. At low shear rate region, the shear rate dependant viscosity decreased dramatically suggesting shear thinning behavior. However, the shear-rate dependant viscosity was found to be nearly independent of shear rate at high shear rates. In addition, lower shear thinning and higher viscosities were observed when the concentration of agar was increased.

Introduction

Chitosan, 1, 4 linked 2 amino, 2 deoxy, β -D - glucan, is a polycationic derived from chitin by alkaline deacetylation [1]. Due to the amino groups that chitosan possesses in its chain, it can be dissolved in dilute aqueous acid solutions, such as acetic acid and propionic acid. Since it is inexpensive, non-toxic and possesses potentially reactive amino functional groups, chitosan has been evaluated for numerous applications, including, medicine, food, cosmetics and waste water treatment [2-6].

Agar, an unbranched polysaccharide, is a hydrophilic colloid extracted from the family of seaweeds (Rhodophyceae). Chemically, agar is a polymer made up of subunits of the sugar galactose [7]. Polysaccharides of the agar group usually contain fewer sulfates than carrageenans, which is responsible for good gelling ability [8]. The most important property of agar is its ability to form reversible gels simply by cooling hot aqueous solutions due to the formation of hydrogen bonds [9-11]. Some of its hydrogel blends, such as PVP-agar hydrogel, have been already prepared [12]. Agar has a wide variety of uses in industry. For example, it has been used in the food area (processed cheese, ice cream, bread and soft candy) due to its ability to form hard gels at very low concentration [13, 14].

Polymeric material has been extensively used in our daily life. Recently, natural polymers have becoming more and more important and have been replacing synthetic polymers in many applications [15] because they are renewable resources, nontoxic and inexpensive. In addition, the natural polymers waste is usually biodegradable [16]. In the recent years, polymer blends have received much attention. This is mainly due to the fact that new materials with better physicochemical properties can be observed when the individual components used to blend are compatible [17, 18]. Modification of chitosan by blending with other polymeric materials might be of interest for some applications. The compatibility of chitosan with other polymers may be obtained since chitosan is considered as a strongly interacting polymer [19].

The aim of the present work was to evaluate the physical properties of chitosan/agar mixture by measuring the dynamic viscosity and pH. The behavior of polysaccharides blends was compared with the reference individual component (pure chitosan).

Results and Discussion

The variation of pH of pure chitosan solution and chitosan/agar solutions versus

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temperature is shown in Fig. 1. For all solutions, the values of pH drop dramatically with increasing temperature. However, pH of the chitosan/agar ratio of 60/40 solution is the highest affected solution by temperature while pH of pure chitosan solution is the lowest affected one. This may indicate that increasing agar concentration yields solutions with lower stability of pH values.

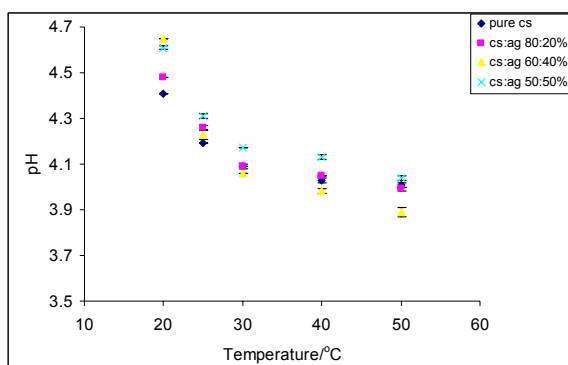


Fig. 1: Influence of temperature on pH of pure chitosan and mixture of chitosan/agar solutions.

The relationship between dynamic viscosity (determined at a constant shear rate) and temperature is demonstrated in Fig. 2. The viscosities of all solutions decrease significantly and linearly with increasing temperature i.e., they are strong function of temperature. The viscosity varies from 158.92cP for 20°C to 94.45cP for 50°C.

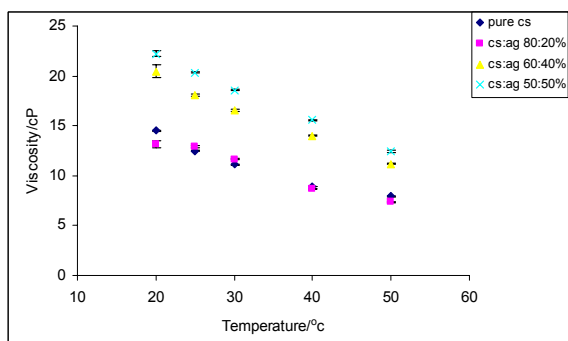


Fig. 2: Influence of temperature on viscosity of pure chitosan and mixture of chitosan/agar solutions at a constant shear rate.

The viscosity values obtained at a constant shear rate can be correlated with temperature according to the Arrhenius equation:

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

where A is a constant related to molecular motion, E_a is the activation energy for viscous flow at constant

shear rate, R is the gas constant and T is the absolute temperature in K.

Fig. 3 presents an Arrhenius plot of the natural log of viscosity versus the inverse of temperature in Kelvins. This graph shows a nearly linear relationship for all solutions. The values of R^2 are 0.983, 0.969, 0.995 and 0.992 for chitosan/agar ratios of 100/0, 80/20, 60/40 and 50/50 respectively. Apparent activation energies of 15.41, 16.52, 15.21 and 15.46 kJ mol⁻¹ were calculated from the slope of the lines. Some values of activation energy of chitosan have been already reported in the literature. For example, [21] revealed that the activation energy varies from 25 kJ mol⁻¹ when DD is 91% to 15 kJ mol⁻¹ when DD is 75% for a chitosan concentration of 20 g L⁻¹ (in 0.2 M AcOH/0.1 M AcONa). Reference [22-24] reported the values of activation energy at zero shear rate vary from about 15 kJ mol⁻¹ to 37 kJ mol⁻¹ for a chitosan concentration ranges between 0 g L⁻¹ and 40 g L⁻¹ respectively (solvent, 0.3 M AcOH/0.05 M AcONa).

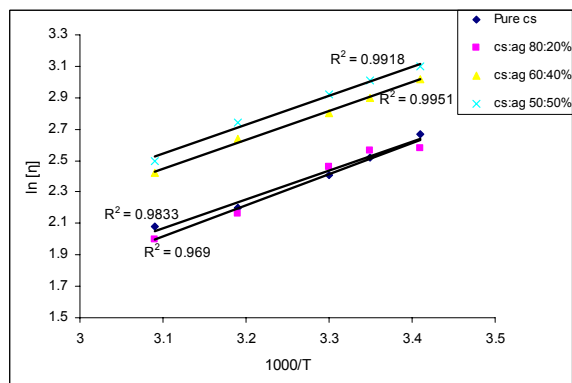


Fig. 3: Arrhenius plots of $\ln \eta$ versus $1/T$ for chitosan and its mixtures with agar.

It is apparent in Fig. 4 that all these types of fluids display decreasing in the dynamic viscosity with increasing shear rate, corresponding to a shear-thinning behavior in the samples. Less shear-thinning and higher viscosity is observed with increasing agar concentration in the solutions i.e. the effect of shear was greater on the ratio 100/0 (pure chitosan) in comparison to the other ratios. This may be due to the enhanced stability of the gel network after blending.

Experimental

Materials

Shrimp source chitosan was purchased from a local company with a deacetylation percentage (DD) of 88.1% defined by UV method [20]. This

chitosan was acid soluble, white-colored and flaky. Agar was purchased from sigma. Acetic acid (glacial 100%, analytical grade) was purchased from Merck (Darmstadt, Germany). Ultra pure water (Maxima Ultra Pure Water, Elga-Prima Corp, UK) with a resistivity greater than 18MΩ/cm was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were used in all experiments.

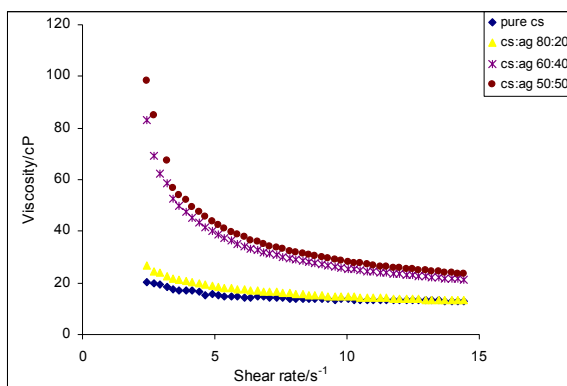


Fig. 4: Influence of the shear rate and concentration on the rheological curves of chitosan/agar aqueous solutions at 25°C.

Preparation of the Solutions

Chitosan was dried in the oven until a constant weight was observed. Then, 5 g of chitosan was dispersed in 500 mL acetic acid (0.1 M) followed by stirring and heating at about 60°C overnight to form 10 g mol⁻¹ chitosan solution. The solution was then filtered to remove dust and other traces of impurities. Air bubbles were eliminated by keeping the solutions at room temperature for some time.

For preparing agar solution, the same procedure as for chitosan was applied with exception of using acetic acid, wherein hot ultra pure water was used. The solution was then stirred and kept at 60°C for 3 h.

Chitosan/agar mixtures were prepared by adding an aqueous agar solution drop by drop into the chitosan solution, which was kept on a magnetic stirrer, at about 90°C and the mixture was stirred at moderate speed for 30 min.

Characterization

The molecular weight of chitosan was about 5.5 × 10⁵ g mol⁻¹ determined by gel permeation chromatography (GPC) equipped with a Waters 1515

HPLC Pump and a Waters 2414 Refractive Index Detector. The column used was PL aquagel-OH 30 (8 μm, 300 × 7.5 mm) and the solvent used was 1% acetic acid.

pH measurements were performed using a microprocessor pH meter (pH 211, Hanna Instruments). Experiments were carried out in triplicate at 25°C and the average and standard deviation values were reported.

Viscosity of chitosan solutions and chitosan/agar mixtures 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 16 mL of sample and the shearing time was 15 s. Viscosity values were reported in centipoises (cP) units. Each measurement was recorded as an average value of five readings.

Conclusion

This study has shown that the ratio 60/40 of chitosan/agar mixtures is the highest affected solution by temperature in terms of pH while pure chitosan solution was the lowest affected one i.e. chitosan/agar blends exhibited less stability of pH as a function of temperature. By plotting the natural log of viscosity against the inverse of temperature, all solutions were found to obey the Arrhenius relation to different degrees. The blend 80/20 recorded the highest value of activation energy while the ratio 60/40 had the lowest one. It was also observed that all solutions exhibited shear thinning behavior when the viscosity was plotted against shear rate. However, lower shear thinning and higher viscosities were observed when agar content was increased.

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