Some Physicochemical Measurements of Chitosan/Starch Polymers in Acetic Acid-Water Mixtures

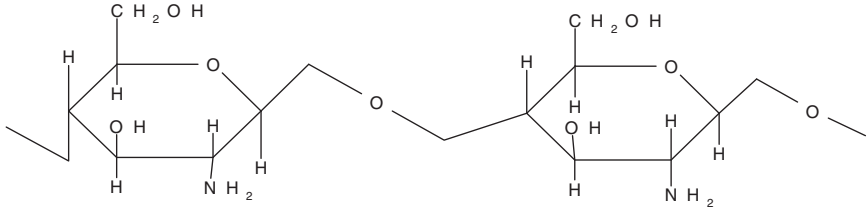
Virpal Singh, Kamlesh Kumari*

Summary: Physicochemical properties of chitosan/starch solution have been studied. Chitosan/starch solutions of different concentrations (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90) are prepared in dilute acetic acid solution (1%, 2%, 3%, 4%). It is observed that the solution of chitosan/starch is miscible over entire range of concentration. The solution properties such as viscosity, density and refractive index are measured. The influence of concentration of solution and speed of rotation on shear stress and shear rate are also determined for polymer solution.

Keywords: density; flow behavior index; refractive index; shear rate; shear stress; viscosity

Introduction

Chitosan is a modified natural carbohydrate polymer prepared by the partial N-deacetylation of chitin. Chitosan is the deacetylated derivative of chitin which is a water insoluble polymer. Chitosan is a natural polycation, nontoxic, biocompatible and biodegradable material. Chitin is an abundantly available natural biopolymer found in the exoskeletons of crustacean like shrimp, crabs, lobster and other shellfish.[1–3] Chitosan dissolves readily in dilute solutions of most of organic acids including malic, acetic, tartaric, glycolic, citric and ascorbic acid solution.[4] It consists of an amino group which exhibits protonation under acidic condition. Chitosan is also found in some microorganisms like yeast and fungi. The primary unit in the chitin polymer is 2-deoxy-2-(acetylamino) glucose. These units are combined by ß-(1, 4) glucosidic linkages forming a long chain linear polymer. The degree of hydrolysis (deacetylation) has a significant effect on the solubility and rheological properties of the polymer. Chitosan, when dissolves in acidic solution gives viscous solution. The viscosity determines the extent of penetration of chitosan into fabric structure. The structure of chitosan is essential for the synthetic chemistry in site selective modification due the different reactivities of amino group at C_2 position and the primary and secondary hydroxyl group at C_3 and C_6 positions.[5] Chitosan is used for synthesis of beads,[6] films,[7] etc. The structure of chitosan is shown in Scheme 1.



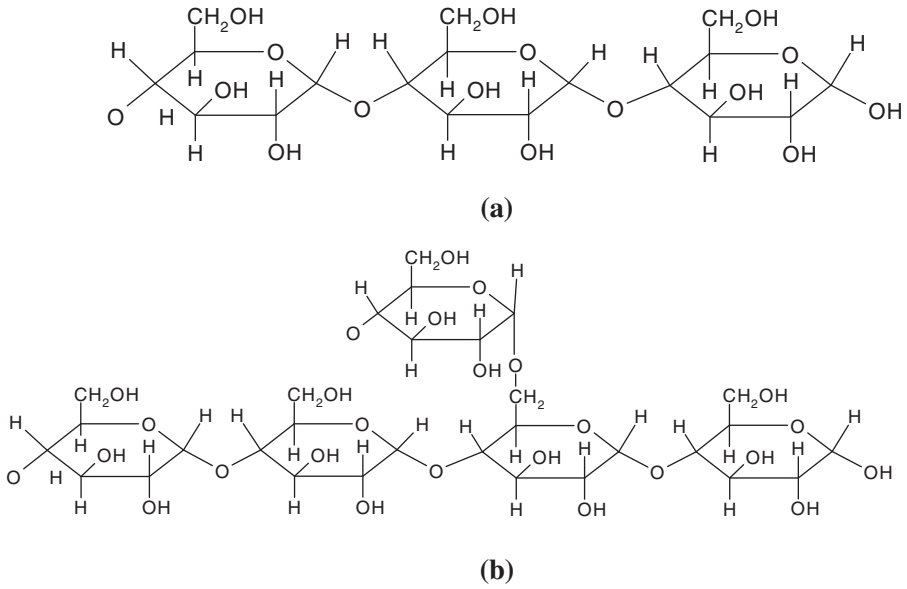
Scheme 1.
Structure of chitosan.

Department of Chemical Technology, Sant Longowal Institute of Engineering and Technology, Longowal, Sangrur (Punjab) 148106, India
E-mail: kamlesh213@yahoo.co.in

Starch is very important natural polymers. It is regenerated by from carbon dioxide and water by photosynthesis in plants. There are many applications such as

in food industry, in agriculture, in medical fields, etc.[8] As a natural carbohydrate, starch is considered to be one of the major constituent of human diet. It is biodegradable and naturally metabolized by human body. Starch obtained from vegetables and food grains such as cassava, corn, wheat, potato, banana, rice, etc.[9] Starch is mainly composed of two homopolymers of D-glucos; amylase and amylopectin. Amylase is mostly linear α-D (1, 4)-glucan and amylopectin has a backbone structure as amylose but with many α-1, 6 linked branch points. Starch has different proportions of amylose and amylopectin ranging from 10–20% amylose and 80–90% amylopectin depending on source. [10–12] Starch occurs naturally as discrete granules since, the short branched amylopectin chains are able to form helical structures which crystallize. Starch granules exhibit hydrophilic properties and strong inter–molecular association via hydrogen bonding formed by hydroxyl groups on the granule surface. [13–17] Linear (a) and crosslinked (b) structures of starch are shown in Scheme 2. The available hydroxyl groups on the starch chains potentially exhibit reactivity specific for alcohols. In other words, they can be oxidized and reduced, and may participate in the formation of hydrogen bonds and ethers. Starch is a renewable, biodegradable, inexpensive, widely obtainable and environmentally friendly material.[18]

The experiments with polymer blends are interesting, since in industry, with variation in the concentration of the polymers, with different properties, a product with some desired characteristics can be obtained. Knowledge of the modification of the viscosity values produced by the utilization of the polymer blends is important because of the effect that it has on the operational cost of several stages of the industrial process. It is important to know the physicochemical properties of chitosan/starch solutions as both polymers find their applications in various fields like drug delivery, bound healing, dressing materials etc.



Scheme 2.
Linear (a) and crosslinked (b) structures of starch.

Experimental Part

Materials

Chitosan is supplied by Fluka Bio Chemica, Germany and starch is purchased from

Himedia (India). Acetic acid (99.5%) is purchased from Merck, Germany. For the preparation of solutions, double distilled water is used.

Preparation of Solution

The solutions of chitosan/starch (ch/st) are prepared in different weight ratios (90/10, 80/20, 70/30, 60/40, 50/50, 40/60) using a balance (Citizen, C × 200) with a precision of 10^{-7} kg. Chitosan has higher molecular weight as compared to starch and both the polymers can't be dissolved in a common solvent due to their different chemical natures. Therefore, both the polymers were dissolved separately in different solvents and mixed together afterwards. The solution of chitosan is prepared by dissolving a known amount of chitosan in 20 ml of aqueous acetic acid (1%, 2%, 3% and 4%) solution at room temperature (25 °C) while stirring for three hours. To prepare a solution of starch a known quantity of starch is dissolved in 20 ml of ultrapure water from Millipore Synergy water system at 95 °C while stirring for one hour followed by cooling. Then both the solutions are mixed together and kept for 24 hours which resulted in a bubble free and clear solution.

Measurements

Viscosity is a measure of fluid resistance to flow. For the determination of viscoelastic properties of polymer solutions, rotational rheometers are perfectly suited. Viscosity of chitosan, starch and ch/st blends in different weight ratios is measured with the help of Brookfield Digital Viscometer (modal Dv-E version 1.00). The principle of operation of the DV-E is to drive a spindle (which is immersed in test fluid) through a calibrated spring. The viscous drag of the fluid is measured by spring deflection. The viscometer is calibrated by using viscosity standard fluid and accuracy was ± 1%. The speed of spindle is fixed at 30, 50, 60, 100 rpm and spindle number (1, 2, 3, 4, 5, 6, and 7) is also fixed according to the nature of the solution. The spindle number 1 is for very low viscous solution and spindle number 7 is used for higher viscous solution.

Density is measured with the help of pychnometer having a bulb volume of 10 cm^3 and a capillary bore with an internal diameter of 1mm. The pycnometer was filled to specific volume with accuracy followed by the measurement of mass of solution.

The measurement of refractive index of 1 g of polymeric sample is done by Abbes refractometer. The scale is adjusted so that the boundary between light and dark halves coincides with the center of the cross hairs. The refractive index on the top scale in the lower part of the viewer is read and recorded.

Results and Discussion

The results are plotted in terms of apparent viscosity versus the concentration of ch(g)/st(g) solution. Figure 1 represents the variation of viscosity of solution with respect to concentration of chitosan. The concentration of acetic acid is varied from 1% to 4%. It is observed that the viscosity of blended solution increases with an increase in concentration of chitosan in solution and decreases with an increase the speed of the rotation. This is due to the fact that chitosan is a high molecular weight

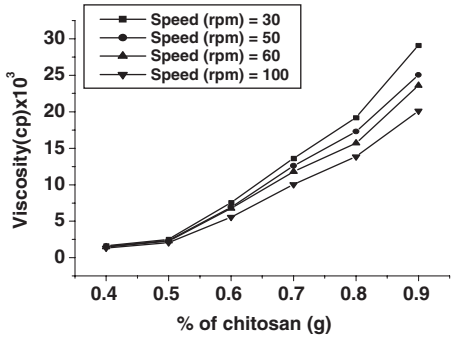


Figure 1.
Variation in viscosity of polymer solution with concentration of chitosan in 2% of acetic acid solution and spindle speed.

polymer as compared to starch and a small increase in the mass of this polymer results in more viscous polymer solution. The decrease in viscosity with increase in the rpm of spindle is due to the enhanced rate of shear stress. As the speed of the spindle increases shear stress increases which results in an increase in shear rate. The density of different solutions is also measured at room temperature (25 °C) (Figure 2). It is noticed that there is an appreciable increase in the density of polymer with increase in concentration of solvent as well as concentration of chitosan. The refractive index of solution increases with increasing % of acetic acid (Figure 3).

Steady Shear Viscosity

In order to describe the steady-shear rheological properties of samples, the data was fitted to the well known Power Law model.

$$\sigma = K\,\dot{\gamma}^{n}$$

Where σ = shear stress; Pa; K = consistency coefficient; Pa sec; $\dot{\gamma}$ = shear rate; sec^{-1}; n = flow behavior index, dimensionless.

Apparent viscosity can be expressed as

$$\eta = \sigma/\dot{\gamma}$$

In applying the Mitschka method, the flow behavior index can be measured from the slope of the logarithm of shear stress versus logarithm of rotational speed plot.[19–22]

$$n = d(\log_{10}\sigma)/d(\log_{10}N)$$

Where σ = shear stress, Pa, N = rotational speed, rpm.

The flow behavior index (n) and consistency coefficient are obtained by plotting graphs between log (shear stress) and log (shear rate) for different solutions prepared in the predefined compositions. The obtained values of consistency coefficient and flow behavior index are given in Table 1. The value of n for ch/st solutions (0.4/0.6%) in 2% acetic acid is found to be 0.595. The values of n indicate that the solutions are highly pseudo plastic in nature and this may be assigned to deviation from Newtonian behavior due the presence of entanglements. It is observed that all the blended compositions exhibit non-Newtonian behavior with increasing chitosan concentration. Rheograms of all the blends are found to lay between the rheograms of pure chitosan

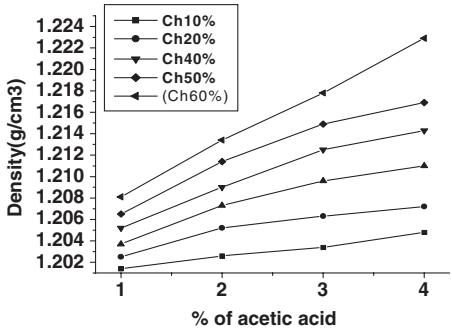


Figure 2.
Dependence of density of solution on chitosan concentration and percentage of acetic acid solution.

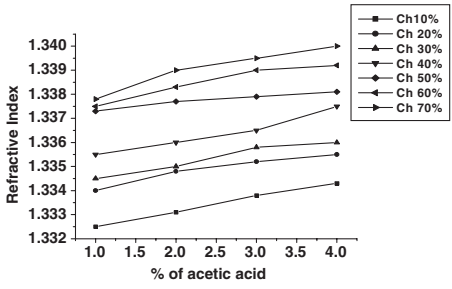


Figure 3.
Dependence of refractive index of polymer solution on chitosan concentration and percentage of acetic acid solution.

Table 1.
Flow behavior index (n) and consistency coefficient for 2% acetic acid solution.

Ch (g)/st (g)	Flow behavior index (n)	Log (consistency coefficient) = log (K)
0.4/0.6	0.595	0.511
0.5/0.5	0.521	0.847
0.6/0.4	0.588	1.721
0.7/0.3	0.742	1.199
0.8/0.2	0.764	1.2180
0.9/0.1	0.701	1.5910

and pure starch components over the entire range.

An increase in shear stress is observed with an increase in speed of spindle (Figure 5). One can see that as the mass of chitosan increases in ch/st solution the shear stress increases which further affect the shear rate.

As the amount of chitosan increases in ch/st solution, the shear rate decreases (Figure 6). The speed of the spindle increases the shear rate linearly for the different ch/st solutions. Generally, shear thinning with higher viscosity is observed with chitosan concentration. Much, [23] Delben et. al., [24] and Kjonisken et al. [25] reported stronger shear thinning at higher concentration for different systems. This is probably attributed to increasing intermolecular entanglement as chitosan concentration increases, which in terns leads to more restricted movement of the individual polymer chains.

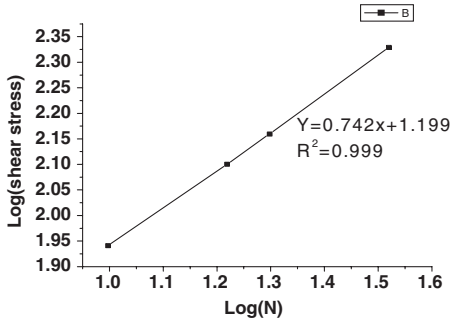


Figure 4.
Influence of spindle speed on shear stress for 2% acetic acid solution of ch/st (0.7/0.3).

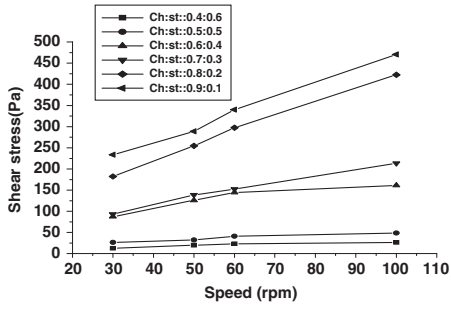


Figure 5.
Influence of spindle speed on shear stress of solution having different concentrations at 25 °C.

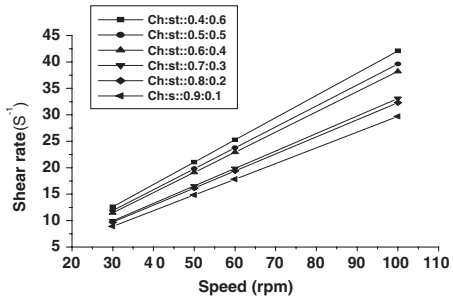


Figure 6.
Influence of spindle speed and solution concentration on shear rate for 2% acetic acid solution of ch/st at 25 °C.

Conclusion

A small increase in the quantity of chitosan produces an enormous effect on solution viscous. The viscosity increases due to the entanglement of the long polymer chains. As the speed of spindle rotation increases, the viscosity of solution decreases due to the disentanglement of polymer chains. It is observed that the blend of ch/st exhibits a non-Newtonian behavior. Further, the pseudo-plasticity increases with an increase in concentration of chitosan. As the concentration of chitosan increases in the blend, the density and refractive index of solution increase. It is also observed that the shear stress and shear rate increase linearly with speed of rotation and concentration of chitosan. The finding of this study may be useful for several industrial processes such as mixing and fluid transport.

[1] J. C. Salamone, *Concise polymeric material encyclopedia*, CRC PRESS, London **1999**, 238–246.
[2] M. N. V. R. Kumar, *React. Funct. Polymers*, **2000**, *46*(1), 1–27.
[3] M. Rinaudo, *Prog. Polym. Sci.*, **2006**, *31*, 603–632.
[4] P. Chen, Y. Hwang, T. Kuo, F. Liu, J. Lai, H. Hsieh, *J. Med. Biol. Eng.*, **2007**, *27*(1), 23–28.

[5] J. Xu, S. P. McCarthy, R. A. Gross, D. L. Kaplan, *Macromol.* **1996**, *29*, 3436–3440.
[6] M. Rani, A. Agarwal, Y. S. Negi, *J. Biomater. and Nanobiotech.* **2011**, *2*, 71–84.
[7] D. R. Lu, C. M. Xiao, S. J. Xu, *Express Polym. Lett.*, **2009**, *3*(6), 366–375.
[8] A. G. B. Pereira, A. T. Paulino, A. F. Rubira, E. C. Muniz, *Express Polym. Lett.*, **2010**, *4*(8), 488–499.
[9] T. N. Baran, F. J. Mano, L. R. Reis, *J. Mater. Sci.: Mater. Med.*, **2004**, *15*, 759–765.
[10] D. P. Chattopadhyay, M. S. Inamdar, *Int. J. Polym. Sci.* **2010**, *2010*, 1–7.
[11] F. Atyabi, S. Manoochehri, S. H. Moghadam, R. Dinarvand, *Arch. Pharm. Res.* **2006**, *29*(12), 1179–1178.
[12] H. Ghania, P. Gilles, *Pharm. Research*, **1990**, *16*(6), 867–875.
[13] Y. Hülya, B. Ceyhun, *J. Polymers and the Environ.* **2003**, *11*(3), 107–113.
[14] E. A. Ei-hefian, H. A. Yahaya, *Maejo Int. J. Sci. Technol.* **2010**, *4*(2), 210–220.
[15] M. D. Kurkuri, A. R. Kulkarni, M. Aminabhavi, *J. of Appl. Polym. Sci.* **2002**, *86*, 526–529.
[16] S. Maity, ''*Analysis and characterization of polymers*'' *Anusandhan Prakashan Midnapore*, **2003**, 85–94.
[17] C. Elvira, J. F. Mano, J. San Roman, R. L. Reis, *Biomater.* **2002**, *23*, 1955–1966.
[18] Z. Wang, X. Fu, S. Li, K. Li, J. Huang, *J. Polym. Mater.* **2010**, *27*(3), 283–292.
[19] P. Mitschka, *Rheo. Acta*, **1982**, *21*, 207–209.
[20] R. K. Wanchoo, A. Thakur, . Sweta, *Chem. Biochem. Eng Q.* **2008**, *22*(1), 15–24.
[21] Y. F. Tang, Y. M. Du, X. W. Hu, X. W. Shi, J. F. Kennedy, *Carbohydr. Polym.* **2007**, *67*, 491–499.
[22] E. A. El-hefian, M. M. Nasef, A. Yahaya, R. A. Khan, *J. Chil. Chem. Soc.* **2010**, *55*, 130–136.
[23] M. Much, *Macromol. Chem. Phys.* **1997**, *198*, 471–484.
[24] F. Delben, R. Lapsin, S. Pircl, *Int. J. Biol. Macromol.* **1990**, *12*, 9–13.
[25] A. L. Kjoniksen, B. Nystrom, C. Iversen, T. Nakken, O. Palmgren, T. Tande, *Langmuir*, **1997**, *13*, 4948–4952.

