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PHYSICOCHEMICAL PARAMETERS STUDY OF CHITOSAN-STARCH-GLUTARIC ACID IN ACETIC ACID-WATER MIXTURES

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Abstract

Knowledge of the physicochemical parameters 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 Chitosan/starch solutions of different variable concentrations from (90/10 to10/90) are prepared in dilute acetic acid solution (1%). Glutaric acid solution concentration is 1% fixed. The solution properties such as viscosity and refractive index are measured. Viscosity of Chitosan-Starch-Glutaric acid solution is measured by Brookfield viscometer modal DV-E version 1.00 and refractive index is also measured by Abbes refractometer. The influence of concentration of solution and speed of rotation on shear stress are also determined for polymer solution.

***Keywords: Chitosan, starch, Glutaric acid, refractive index, viscosity*.**

INTRODUCTION

Chitosan is inert, hydrophilic, and biocompatible and biodegradable and possesses mucoadhesive properties (Rinaudo, 2006; Dutta at et, 2004; Rinaudo et al, 1999; Chattopadhyay and Inamdar, 2010). Chitosan,(1, 4)-[amino-2-deoxy-β-D-glucan] has amine side group, which is responsible its polycationic character, and formation of well-known intermolecular complexes with carboxylic acid and poly carboxylic acid (Hashemi Doulabi et al, 2013). Chitosan is the biopolymer obtained from deacetylation of chitin (Rinaudo, 2006). Chitosan is multifunctional polymer and due to its unique and versatile biological properties (Hejazi and Amiji, 2003). This is useful compound in medical and pharmaceutical fields (Szymańska and Winnicka,2015).Chitosan and Starch are polymers that can be obtained from renewable sources, which have producing qualities films (Silva-Pereira et al., 2015), beads, nano particles and also many other applications. Starch, a polymer of α-D-glucose, composes of two forms of glucose polymers, linear (amylose) and branched chain (amylopectin). Starch occurs in many plant species in the form of spherical granules. Amylose is a linear homopolymer of α (1, 4)-linked glucose with a degree of polymerization of ~1000. Amylose makes up ~35% of starch (range of 11-36% depending on plant and organ) and amylopectin is highly branched form of "amylose" which has α (1, 6) glycosidic linkages (Atyabi et al, 2006; Chattopadhyay and Inamdar, 2010). It can form complex with fat or iodine because the core of the amylose helices is hydrophobic molecule. Amylopectin is large size polymer molecule of starch, which is the main component of the starch granules. It is highly branched and 4-5% of its glucose monomers contain a 1-6 linkage (Wang et al., 2010). 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.

PREPARATION OF BLENDED SOLUTION

Chitosan low viscous (loss on drying < 10 % ash, Insoluble matter > 1 %, viscosity < 200 m Pa s) was supplied by FlukaBio Chemica (Germany) and corn starch procured from Himedia (India). Acetic acid (99.5 %) was purchased from Merck (Germany).Glutaric acid was received from Sigma-Aldrich (Germany). For the preparation of solutions double distilled water was used to prepare all solutions.

Chitosan has higher molecular weight as compared to starch and both polymers cannot be dissolved in a common solvent due 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%) solution at room temperature (25 ^{0}C) stirring for three hours. To prepare a solution of starch a known quantity of starch is dissolved in 20 ml ultrapure water from Millipore synergy water system at 95 ^{0}C heating with stirring till 20 minutes followed by cooling. Afterwards, both solution of chitosan and starch are mixed together while stirring to produce a blended solution and kept for 24 hours which resulted in a bubble free and clear solution. Then 1ml of glutaric acid of 1% is added in all blended solution for whole study. Table 1 shows the designated composition for all the solutions prepared in this study. The range of concentration of both the polymers selected so as to produce compatible blends.

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Table 1 Composition of chitosan and starch blended solution

	Chitosan Solution		Starch Solution	
S.No	Ch(g)	AA*(ml)	St(g)	Water(ml)
1	0.4	20	0.6	20
2	0.5	20	0.5	20
3	0.6	20	0.4	20
4	0.7	20	0.3	20
5	0.8	20	0.2	20
6	0.9	20	0.1	20

*Acetic acid concentration= 1% and Glutaric acid concentration=1%.

MEASUREMENT OF VISCOSITY

Viscosity is a measure of fluid's resistance to flow. Viscosity of pure chitosan and pure starch, chitosan-starch blends with different ratios were determined using 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 was calibrated using viscosity standard fluid and accuracy was ±%1. The viscosity and torque values are reported in centipoises (cp) and dyne cm respectively. The speed of spindle is fixed at 30, 50, 60,100 rpm and spindle number (1, 2, 3, 4, 5, 6, and 7) are fixed according to viscosity of the solutions. The spindle number 1 is for very low viscous solution and spindle number 7 is very high viscous solution.

FLOW BEHAVIOUR ANALYSIS OF BLENDED SOLUTION

The rheological behaviour is studied using following Power law model that satisfactorily fitted the experimental data.

$$\sigma = K\gamma^{n} (1)$$

Where σ is the shear stress, $\dot{\gamma}$ is the shear rate, K is a characteristic constant of the fluid, and n is the flow index. The consistency index K is defined as the shear stress at a shear rate of 1.0 s-1 and the flow behavior index n is dimensionless reflecting the closeness to Newtonian flow. If n = 1, the fluid is Newtonian (Rao, 1999).

According to the Mitschka method, the flow behavior index can be found from the slope of the logarithm of shear stress verses logarithm of rotational speed plot. The flow behaviour can be determined by the following relation:

$$n = \frac{d(\log_{10} \pm)}{d(\log_{10} N)} (2)$$

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

The flow behaviour index (n) is obtained by plotting graphs between log (shear stress) versus log (N) for different solutions.

REFRACTIVE INDEX MEASUREMENT

The measurement of refractive index of 1 g polymeric sample was done by Abbes refractometer. Refractive index for sodium D-line is measured to an uncertainty of 0.0001 with thermostatically controlled refractometer. The scale is adjusted so that the boundary between light and dark coincides with the centre of the cross hairs. The refractive index on the top scale in the lower part of the viewer was read and recorded of each solution.

RESULTS AND DISCUSSION

Measurement of viscosity

Viscosities of various compositions are measured by Brookfield viscometer. The graph is plotted between the viscosity and chitosan-starch-glutaric acid concentration

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in figure 1. The figure 1 shows that 1% solution of acetic acid; the viscosity is increasing with increasing chitosan (g) content in the solution of chitosan-starch the viscosity increases due to entanglement of the long polymer chain. The viscosity decreases with increasing speed of the rotation of spindle because the entangled polymer chain becomes disentangles polymer chain and increasing with increasing chitosan(g) content in the solution of chitosan-starch and as the viscosity is decreasing when content of starch the increasing the solution of chitosan-starch.

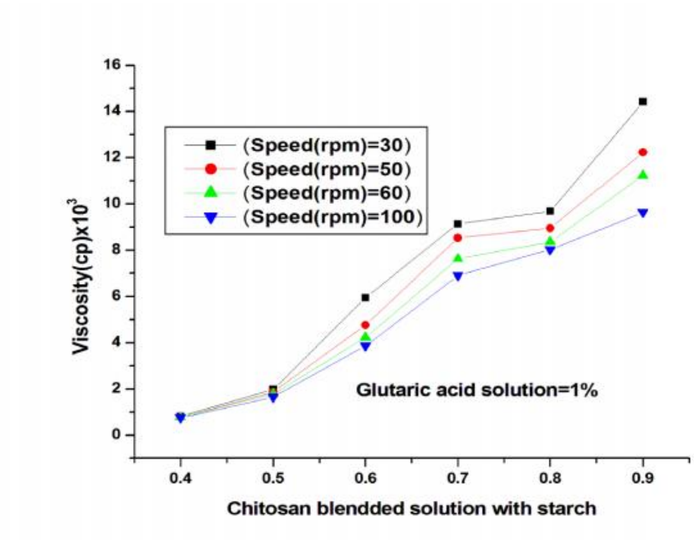

Figure 1: Variation in viscosity of polymer solution with concentration of chitosan in 1% of acetic acid solution and spindle speed.

Measurement of Refractive index of Glutaric acid-chitosan-starch solution

The study of the refractive index is done according to the variation in compositions and variation of acetic acid 1% the figure 2 shows that the refractive Index versus% of varies chitosan/starch (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90) at 25 0C temperature . The graph shows refractive index increases with increasing % of chitosan for 1% acetic acid solution

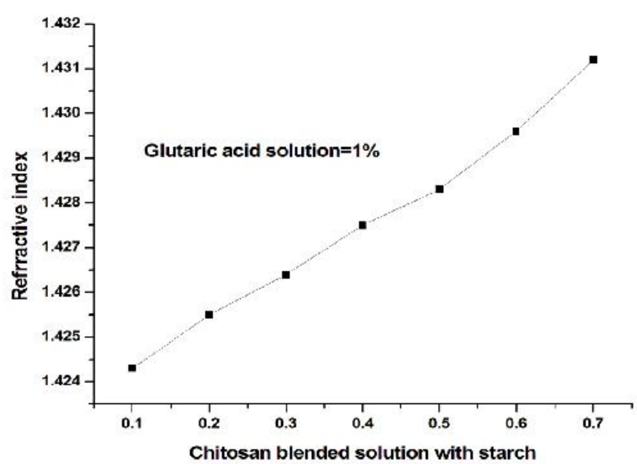

Figure 2 Dependence of refractive index of polymer solution on chitosan concentration

Measurement of flow behavior index of Glutaric acid-chitosan-starch solution

It is observed that the flow and viscosity plots are straight lines indicating that the Ostwald-de Wale equation (Power law model) is applicable given in equation 1.2.

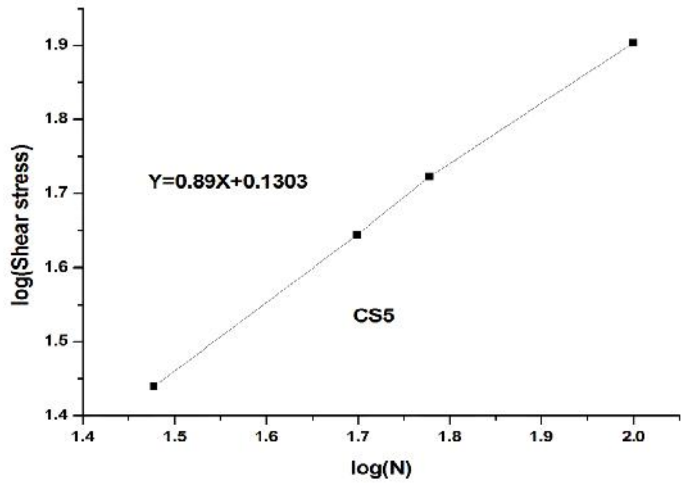

Fig 3 Influence of spindle speed on shear stress for 1% acetic acid solution of (CS5).

The flow behaviour index (n) and consistency coefficient are obtained by plotting graphs between log (shear stress) versus log (shear rate) for different solutions. These values of n indicated that the both solutions are highly pseudo plastic in nature to assign deviation from Newtonian behaviour due the presence of entanglements (Wanchoo et al, 2008). However, solution of 1 % acetic acid (chitosan/starch) approaches nearly Newtonian behaviour (n = 0.92). It is observed that all the blend compositions exhibit non-Newtonian behaviour with increasing chitosan concentration.

Table 2 Flow behavior index (n) for different compositions

S.No	C(g)	S(g)	Flow behaviour index(n)
			1% of Acetic Acid
1	0.4	0.6	0.92
2	0.5	0.5	0.89
3	0.6	0.4	0.776
4	0.7	0.3	0.744
5	0.8	0.2	0.737
6	0.9	0.1	0.688

CONCLUSIONS

Increasing chitosan concentration in a chitosan/starch solution, the viscosity increases due to entanglement of the long polymer chain and speed of spindle rotation increases, as viscosity decreases at room temperature because the entangled polymer chain becomes disentangles polymer chain. With increasing chitosan concentration and refractive index of chitosan/starch blend also increases. The flow behavior index shows nearly Newtonian. The pseudo plasticity is increasing with increasing chitosan concentration nearly Newtonian. The pseudo plasticity is increasing with increasing chitosan concentration.

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