

Rheological and Morphological Studies of Chitosan/agar/ Poly (Vinyl Alcohol) Blends

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Abstract: In this study, a number of ternary mixture aqueous solutions of chitosan/agar/poly vinyl alcohol (CS/AG/PVA) at different proportions (considering chitosan as the main component) were prepared. The effects of temperature, shear rate, shearing time and storage time on the rheological properties, i.e., the apparent viscosity and the shear stress as a function of shear rate were investigated for the ternary system. Results showed that a Newtonian behavior was observed at temperatures from 40°C to 55°C for the ratios 90/05/05 and 80/10/10. The mixture solutions become pseudoplastic (shear thinning) when the concentrations of agar and PVA were higher than 10 % each. It was also found that all the blend solutions obeyed the Arrhenius equation. In addition, the effect of the shearing time on the shearing viscosity did not show any significant change at all shearing times applied for lower concentrations than 15% of each of agar and PVA in this study. However, at higher concentrations of agar and PVA, a rheopectic behavior was observed. Furthermore, different behaviors were observed for the blend solutions when the period of storage was extended to three weeks. The observations obtained from the rheological measurement suggested the existence of interaction between the three polymers. Finally, the morphology of the blended films confirmed the interaction between the functional groups of the blend components.

Key words: chitosan, agar, poly (vinyl alcohol), blending, rheology, morphology

INTRODUCTION

Chitosan, a natural polysaccharide, has recently attracted much attention in different parts of the world. It is obtained by alkaline deacetylation of the second most abundant naturally occurring chitin of crab and shrimp shells^[1]. Due to the presence of amino groups in its chain, chitosan 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 widely used in the fields of medicine, food, cosmetics, agriculture, wastewater treatment and so on^[2-6].

Agar, an unbranched polysaccharide, is a hydrophilic colloid extracted from the family of seaweeds (Rhodophyceae). 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^[7,8]. 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^[9,10].

Poly (vinyl alcohol) (PVA) is a non-toxic, water-soluble synthetic polymer that has been commercially produced on a large scale. It has a large number of hydroxyl groups which allows it to react with many types of functional groups. This advantage makes it suitable as biocompatible materials. PVA has been widely utilized in diverse fields, ranging from thickening agent to controlled release systems^[11].

Polymer blending has received much attention in the recent years. This is mainly due to the fact that new materials with better physicochemical properties can be observed when the original polymers are compatible^[12,13]. Blending of synthetic with natural biopolymers is considered as a new class of materials that is of particular significance^[14]. Since chitosan has many functional groups, modification of chitosan by blending with other polymeric materials is expected to be useful for some applications. Blending of chitosan with Poly (vinyl alcohol) has been already reported in literature^[15-20]. However, study of CS/AG/PVA blends is still rare. The structure of chitosan, agar and poly (vinyl alcohol) is shown in Figure 1.

This work was intended to investigate the rheological properties, i.e., effects of shear rate, temperature, shearing time and storage time on the

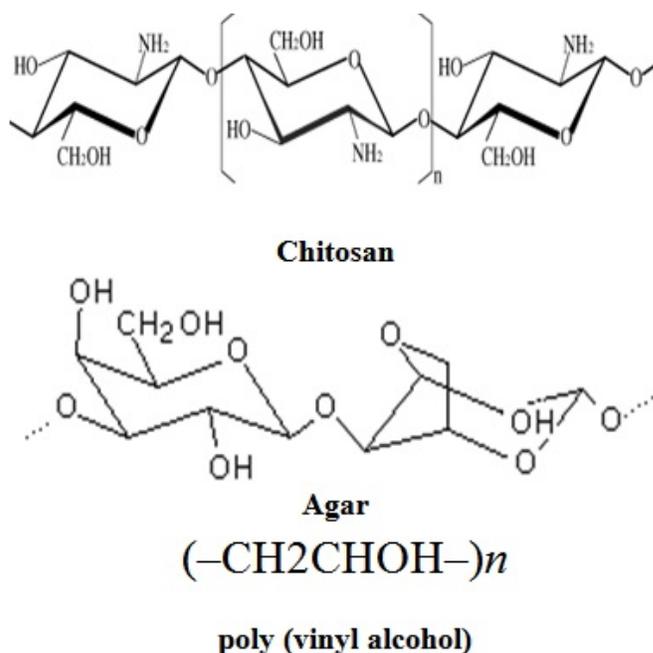


Fig. 1: The chemical structures of chitosan, agar and poly (vinyl alcohol).

apparent viscosities and shear stresses of aqueous solutions of CS/AG/PVA at different proportions. It is also aimed at studying the morphology of the blended films.

MATERIALS AND METHODS

Materials: Shrimp source chitosan with a degree of deacetylation (DD) of 88.1% determined by UV method [21] was purchased from a commercial source. The agar was purchased from Sigma and its average molecular weight was 1.3×10^4 g mol⁻¹. The PVA Fluka (56-98) had an average molecular weight of 195×10^3 g mol⁻¹. Acetic acid (glacial 100%, pro-analysi) 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.

Preparation of CS/AG/PVA Ternary Blended Solutions: 10 g L⁻¹ solution of chitosan was prepared by dissolving 5 g of chitosan in 500mL acetic acid (0.1M) followed by stirring and heating at 60°C overnight. The solution was filtered to remove dust and other traces of impurities. Air bubbles were eliminated by keeping the solutions at room temperature for 2 h. A similar 10 g L⁻¹ solution of AG as well as PVA were prepared by dissolving 5 g in 500mL preheating ultrapure water. The solutions was then stirred and kept at about 90°C for 2 h. Then, CS and AG solutions were blended together under continuous stirring at

around 94°C for 30 min to form a homogenous blend solution. Finally, CS/AG and PVA solutions were homogeneously blended at 94°C for 30 min to form a ternary blended solution. The compositions of CS/AG/PVA ternary blends are shown in Table 1.

Table 1: The different compositions of the chitosan, agar and PVA ternary blends

Blending ratio (CS/AG/PVA)	(wt %) _{CS}	(wt %) _{AG}	(wt %) _{PVA}
90/05/05	90	5	5
80/10/10	80	10	10
70/15/15	70	15	15
60/20/20	60	20	20
50/25/25	50	25	25

Preparation of CS/AG/PVA Ternary Blended Films:

The ternary blended solutions were poured onto polystyrene petri dishes followed by drying at 60°C for 48 h. The resultant blended films were peeled off gently and kept under evacuated desiccator over fresh silica gel until use. All films obtained were transparent and free of air bubbles.

Methods:

Molecular Weight Measurements: The molecular weight of chitosan was about 5.5×10^5 g mol⁻¹ determined at 30°C 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. The GPC was calibrated using pullulans as standard.

Viscosity Measurements: A Brookfield digital viscometer, model DV-II + Pro, with an attached UL adapter was used to describe the rheological characteristics of the blend solutions in this work. The viscosity was determined in 20 mL of the sample and the shearing time was 15 seconds. For the storage time measurements, solutions were kept at room temperature in glass bottles in a dark place until analysis. Each measurement was recorded as an average value of five readings when a constant shear rate was applied.

Scanning Electron Microscopy: The surface morphology of the samples was investigated using SEM. A digital Leica S440 scanning electron microscope was used in order to quantify the surface smoothness and homogeneity.

RESULTS AND DISCUSSION

The Effects of Temperature on the Apparent Viscosity of CS/AG/PVA Blended Solutions: The shear rate-dependent viscosity of CS/AG/PVA mixture solutions as a function of shear rate at a temperature range of 45°C to 55°C is presented in Figure 1 (Higher temperatures were not applied in order to avoid thermal degradation of the polymers and solvent evaporation while lower temperatures could not be applied due to the gel formation for some mixtures). The Newtonian behavior is observed at all temperatures for the ratios 90/05/05 and 80/10/10. However, the increase in apparent viscosity and the appearance of shear thinning behavior begin to appear at the ratio 70/15/15 and it is more clearly at higher compositions of agar and PVA. It was reported that the occurrence of strong polymer-polymer interaction in a solution can be noticed by increasing in the solution viscosity [22]. It is, therefore, expected that the increase in viscosity for CS/AG/PVA blends is attributed to the formation of hydrogen bonding due to the interaction among the functional groups of chitosan, agar and PVA (-OH and -NH₂ groups in chitosan, -OH groups in agar and -OH groups in PVA).

The relationship between the shearing viscosity (determined at a constant shear rate) and temperature for CS/AG/PVA blends is demonstrated in Figure 3(a). This graph shows a nearly linear relationship (Table 2) whereby viscosity of the mixture solutions decreases with increasing temperature, i.e., it is a strong function of temperature. It can also be noted that the most effected ratios by temperature are 6/20/20 and 50/25/25.

The variation of viscosity dependent on temperature at a constant shear rate (6.15 s⁻¹) can be evaluated 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 a constant shear rate, R is the gas constant and T is the absolute temperature in K. Figure 3(b) presents an Arrhenius plot for various proportions of CS/AG/PVA mixture solutions. This graph also shows linear relationships. The values of the apparent activation energy are shown in Table 3.

Knowing the activation energy is important in deducing the sensitivity of a process towards temperature^[23]. The higher the activation energy, the more the sensitive process to temperature. The activation energy is also useful for signifying the minimum amount of energy required for the reactants to start a reaction^[24]. The lower the activation energy, the faster the reaction will proceed. In this work, the activation energy of pure chitosan is 16.79 kJ mol⁻¹. As the concentrations of agar and PVA were increased, the activation energy was decreasing until the ratio of 70/15/15, after which the activation energy started increasing to reach 20.8 kJ mol⁻¹ for the rat

The Effects of Shearing and Storage Time on the Apparent Viscosity of CS/AG/PVA Solutions: The effect of shearing time on the apparent viscosity was studied in this work using various amounts of the components for 15, 30, 45, 60 and 75 seconds at 40°C to study the shearing time effect (Figure 4). For the ratios 90/05/05 and 80/10/10, no significant changes were observed and the apparent viscosity remained almost constant at all shearing times applied. However, the ratios 70/15/15 and 60/20/20 exhibited increasing in the apparent viscosity with increasing shearing time in general, and the solutions became pseudoplastic. This behavior is more obvious for the proportion 50/25/25. Fluids that exhibit increasing in the apparent viscosity with increasing shearing time at a constant shear rate are known as rheopectic^[25]. In addition, different behaviors were observed for the blended solutions when the period of storage was extended to three weeks at a constant shear rate (Figure 5). The pure chitosan solution showed gradual increase in viscosity with time while the proportions 90/05/05 80/10/10, 70/15/15 and 60/20/20 recorded a drastically increase in viscosity within the first week and different in the second and third weeks. However, the blend ratio 50/25/25 recorded the highest value of viscosity (132cP) within the first week, after which the viscosity dropped into about 45cP. This may suggest that the solutions should be used within the first week before starting losing their viscosity. The rapid increase in viscosity with time may indicate that some strong interactions have taken place among the chains of the three polymers.

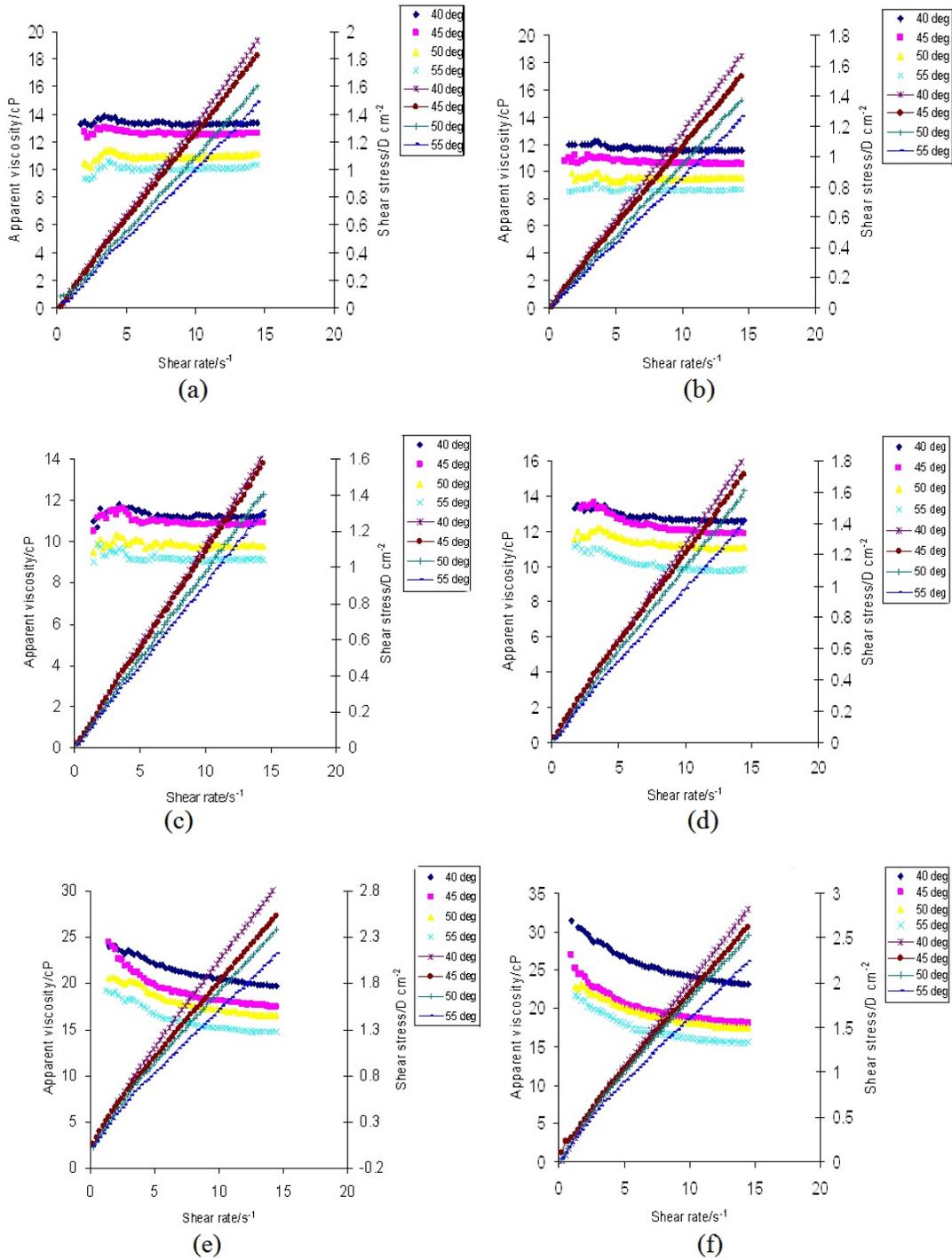


Fig. 2: The influence of the shear rate and temperature on the rheological curves of (a) pure chitosan solution, (b) (90/05/05), (c) (80/10/10), (d) (70/15/15), (e) (60/2/20) and (f) (50/25/25).

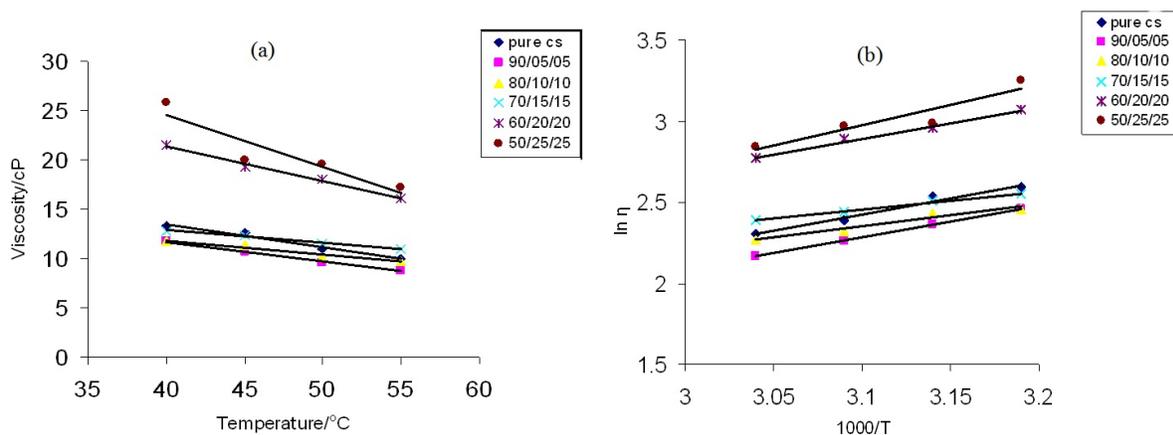
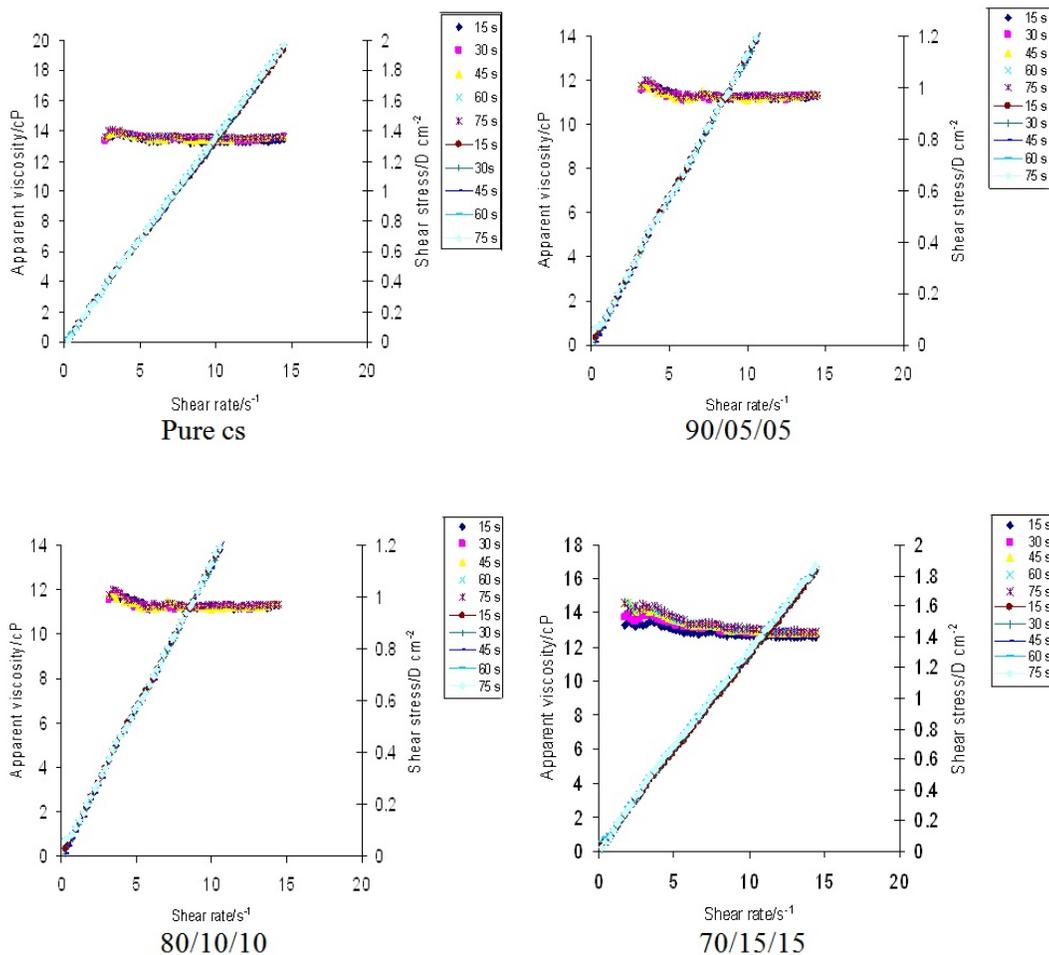


Fig. 3: (a) The Influence of temperature on viscosity of CS/AG/PVA ternary blended solutions at a constant shear rate, and (b) The Arrhenius plot of $\ln \eta$ versus $1/T$ for the ternary blend solutions.



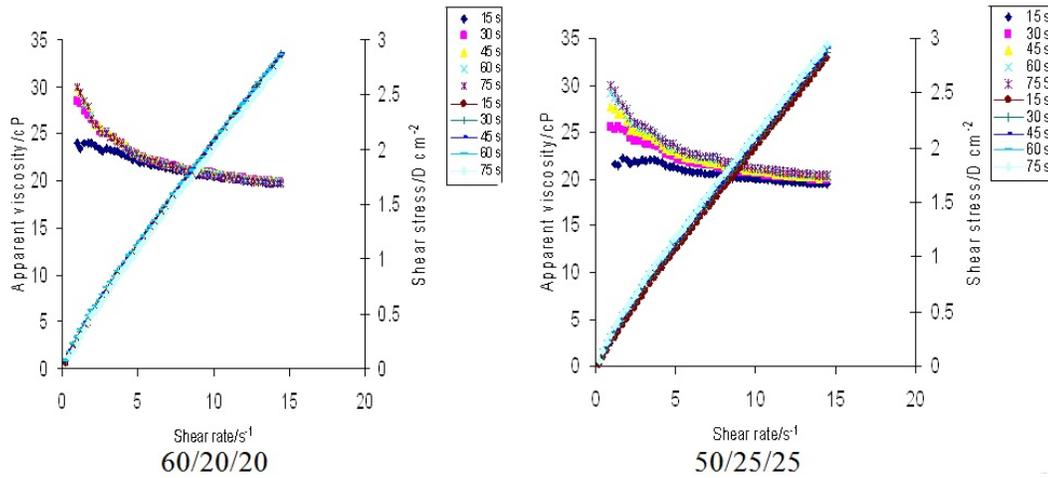


Fig. 4: The influence of the shear rate and shearing time on the rheological curves of (a) pure chitosan solution, (b) (90/05/05), (c) 80/10/10, (d) 70/15/15, (e) 60/20/20 and (f) 50/25/25 at 40°C.

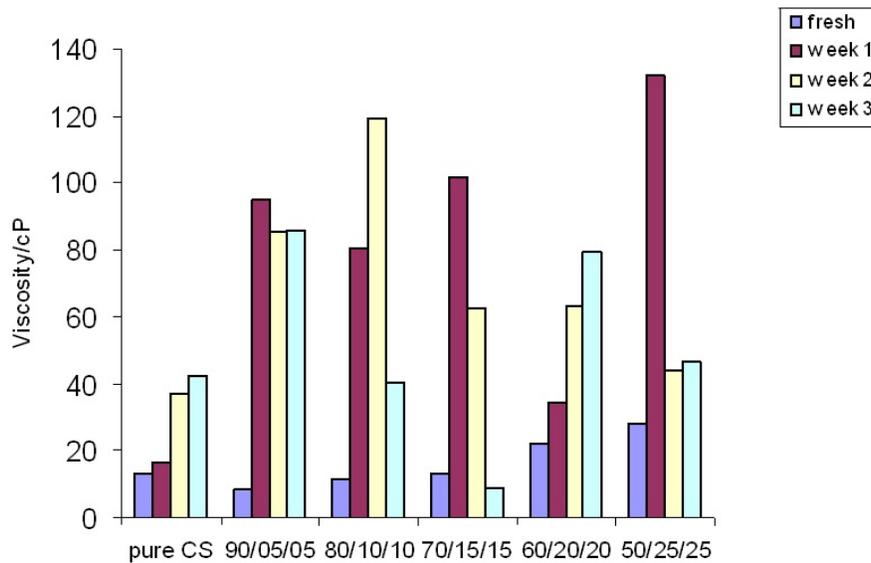


Fig. 5: The effect of storage time on the apparent viscosity (determined at a constant shear rate) of pure CS and CS/AG/PVA ternary blend solutions.

Scanning Electron Microscopy: The SEM photographs of the pure CS film and the CS/AG/PVA blended films at different ratios are shown in Figure 6. As can be seen, chitosan film shows smooth and homogeneous surface with some straps on the top surface. In addition, all blended films displayed clear and homogenous surfaces with no interface layer. However, the ratio 50/25/25 showed a little rougher surface indicating more hydrophilic top surface than the other blend films. According to Chen *et al.*^[26], such a rough surface could be due to the reorientation of polar functional groups toward to the top surface of the ternary blend films. Based on these observations it can be concluded

that all blend films were compatible at all ratios. The formation of homogeneous blends of chitosan, agar and PVA was mostly caused by the interactions of hydrogen bonds between the functional groups of the blend component.

Conclusions: This study has shown that the rheological measurements of the ternary blended solutions of CS/AG/PVA suggest a Newtonian behavior at lower concentrations of agar and PVA and a non-Newtonian behavior at higher concentrations of the two polymers at temperatures between 40°C and 55°C. All blended solutions were found to obey the Arrhenius equation.

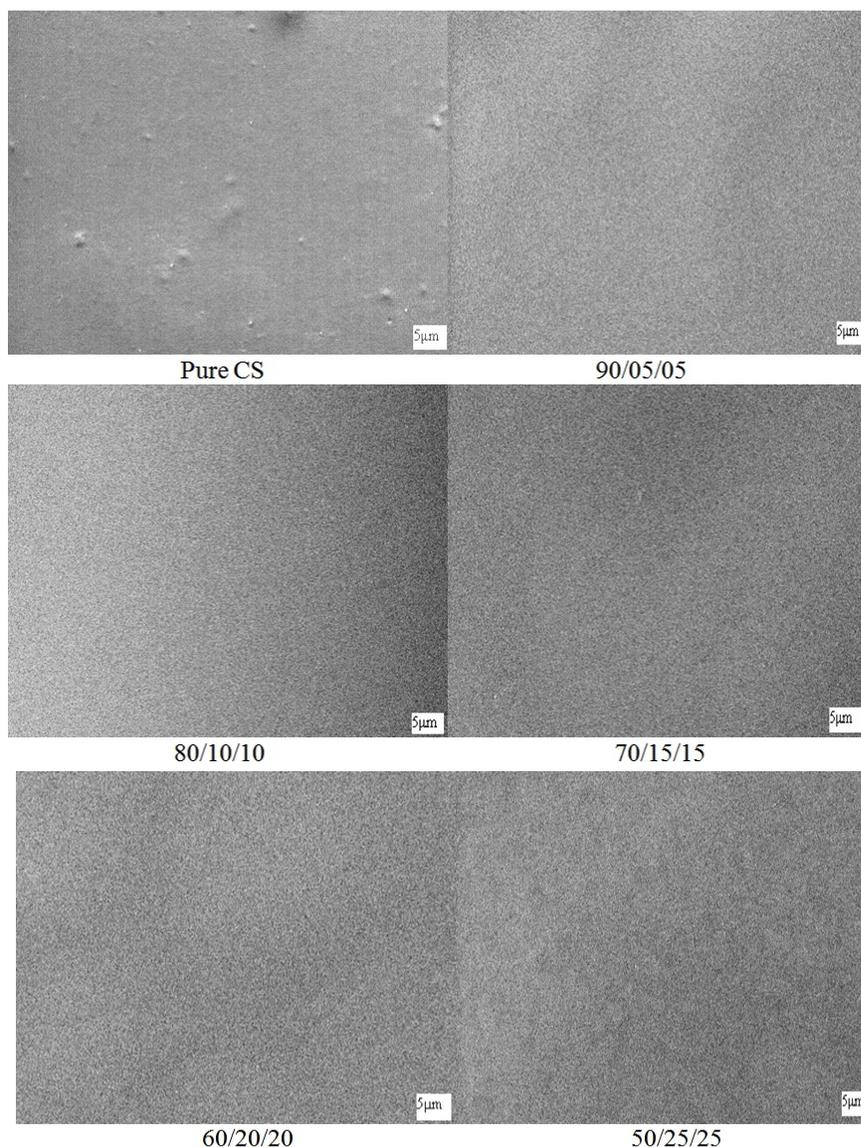


Fig. 6: SEM micrographs of pure CS and CS/AG/PVA ternary blended films (mag = 150X).

Table 2: The relationship between the R^2 and the blend concentration.

CS/AG/PVA	R^2
Pure CS	0.9821
90/05/05	0.9964
80/10/10	0.9553
70/15/15	0.9912
60/20/20	0.9873
50/25/25	0.8648

Table 3: The values of the activation energy of CS/AG/PVA blends

Mixture	E_a (kJ mol ⁻¹)
Pure CS	16.79
CS/AG/PVA 90/05/05	16.13
CS/AG/PVA 80/10/10	11.31
CS/AG/PVA 70/15/15	9.15
CS/AG/PVA 60/20/20	16.13
CS/AG/PVA 50/25/25	20.80

This study has also shown that curves of the apparent viscosity of the ternary system show almost no change in the apparent viscosity at all shearing times of 15-75 s for lower concentrations than 15% of each of agar and PVA. However, a rheopectic behavior was observed at higher concentrations of the two polymers. When the storage period was extended to three weeks, all the ternary blends of CS/AG/PVA recorded an increase in viscosity with time especially in the first week. Based on the above observations, we can conclude that the interaction between the three components has occurred. Finally, the morphology of the blend films showed homogeneous surfaces and confirmed the interaction between the functional groups of the blend components.

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