



Preparation and Characterization of Chitosan/Agar Blended Films: Part 2. Thermal, Mechanical, and Surface Properties

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Abstract: Chitosan/agar (CS/AG) films were prepared by blending different proportions of chitosan and agar (considering chitosan as the major component) in solution forms. The thermal stability of the blended films was studied using thermal gravimetric analysis (TGA). It was revealed that chitosan and agar form a compatible blend. Studying the mechanical properties of the films showed a decrease in the tensile strength and elongation at break with increasing agar content. Blending of agar with chitosan at all proportions was found to form hydrogel films with enhanced swelling compared to the pure chitosan one. Static water contact angle measurements confirmed the increasing affinity of the blended films towards water suggesting that blending of agar with chitosan improves the wettability of the obtained films.

Keywords: Chitosan, Agar, Blend films, Mechanical properties, TGA.

Introduction

Chitosan is a modified carbohydrate polymer derived from chitin, the second most abundant naturally occurring polymer, by alkaline deacetylation. It is a biocompatible, biodegradable, antibacterial and inexpensive natural polymer with good film forming ability, which promotes its use in a variety of interesting applications^{1,2}. Agar is a hydrophilic polysaccharide extracted from the family of seaweeds (Rhodophyceae) that has been extensively used in food industry^{3,4}. One important property of agar is its ability to form reversible gels even at low concentration simply by cooling its hot aqueous solutions. This is due to the formation of hydrogen bonds⁵⁻⁷. Blending of these two polymers is expected to improve some properties of chitosan, such as gelation and swelling properties.

The objective of this study is to prepare chitosan/agar films by physical solution blending of chitosan and agar at different proportions. Properties of various blended films of

chitosan/agar, such as thermal stability, mechanical, swelling and surface (contact angle) properties were investigated in correlation with the agar content in the blended films.

Experimental

Chitosan with a degree of deacetylation (DD) of 88.1% determined by UV method⁸ was obtained from a commercial source. Agar was purchased from Sigma-Aldrich and its molecular weight was 1.3×10^4 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 18M Ω /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 solutions

Chitosan was dried in an oven until a constant weight was observed. A 10 g L⁻¹ solution of chitosan was prepared by dissolving 5 g of chitosan in 500 mL acetic acid (0.1 M) followed by stirring and heating at 60 °C for 16 h. The solution was filtered to remove dust and other traces of impurities. Air bubbles formed in the solution were eliminated by keeping the solutions at room temperature for 2 h. A similar 10 g L⁻¹ solution of agar was prepared by dissolving 5 g in 500 mL preheating ultrapure water. The solution was then stirred and kept at about 75 °C for 3 h.

Preparation of blended films

The preparation of blended films of chitosan and agar was carried out at various proportions. The aqueous agar solution was added drop by drop to the chitosan solution, under continuous stirring at 90 °C in various proportions by volume. The range of the added agar to chitosan solution was from 0-50 vol%. Stirring was allowed to continue for 30 minutes after mixing. Films of the resulting homogeneous solutions were obtained by casting prescribed amounts of the blend solution onto polystyrene Petri dishes followed by drying at 60 °C for 48 h. The films were peeled off and kept under evacuated desiccator over a fresh silica gel until use. All films obtained were transparent and free of air bubbles. Similar films from pure chitosan and agar were prepared using the same casting procedure and used as references.

Film thickness

The film thickness was measured with a digital micrometer (Mitutoyo, Japan) with 0.001 mm resolution. Several thickness measurements were taken at various positions on each specimen and the average values were recorded.

Molecular weight measurements

The molecular weight of chitosan was about 5.5×10^5 g mol⁻¹ determined by gel permeation chromatography (GPC)⁹.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo thermogravimetric analyzer model TGA/SDTA851e. TGA runs were carried out in a temperature range of 40-500 °C, under nitrogen atmosphere, at a constant heating rate of 10 °C/min. The sample size of 4-10 mg was weighed and the mass of the sample containing-pan was continuously recorded as a function of temperature.

Mechanical properties

The mechanical properties were measured by a universal mechanical tester (Instron, Model 5566, USA) according to the ASTM Standard Method D 882-91¹⁰. Dumbbell-shaped

specimens of 50 mm long with a neck of 28 and 4 mm wide were used. The measurements were carried out at 23 °C and 50% relative humidity. The crosshead speed was fixed at 50 mm/min. A minimum of five specimens were tested for each sample.

Degree of swelling

The swelling behavior of the films was measured by equilibrating the blend films in deionized water at room temperature for 10 h. The excess water was removed by blotting the surfaces of the film with a tissue paper and the weight was then recorded. This process was repeated at least three times for each sample. The degree of swelling was calculated using the following equation:

$$\text{Degree of swelling (\%)} = [(W_2 - W_1) / W_1] \times 100$$

Where, W_1 and W_2 are the weights of dried and swollen samples, respectively.

Contact angle measurements

The static water contact angles of the films were measured at room temperature by the drop method using an optical contact angle meter CAM 200 (KSV Instruments Ltd, Helsinki, Finland) to examine the surface wettability of the films. The substrates used for the experiments were glass microscope slides (25.4×76.2 mm, 1-1.2 mm thick). Each slide was cleaned before use by soaking in ethanol overnight. 7 μ L of distilled water was carefully injected on the film surface before measuring and the measurement time was 24 seconds. The contact angles were measured on both sides of the drop and averaged. Each reported contact angle was the mean value of at least 10 measurements.

Results and Discussion

Thermal stability

Figure 1 shows the results of TGA curves of chitosan film, agar film and their blended films. Two weight losses (degradation patterns) are observed in the TGA curve of pure chitosan. The first degradation that starts from 50 °C and continues to above 150 °C in a form of 6% loss in the weight is due to the dehydration. The prolonged weight loss of water above 100 °C is due to the presence of hydrogen bonding between functional groups in both agar and chitosan and water molecules. The second weight loss begins at about 150 °C and the corresponding 52% weight loss is attributed to the decomposition of chitosan main chains. The total weight loss of the sample at about 500 °C is 58%. The remaining residue of the film which equals 42% is mostly due to the formation of inorganic complex containing C, N and O. Similar multi-degradation behavior of chitosan film was reported in the literature¹¹⁻¹³. The TGA curve of agar film shows two distinct zones within the range of investigated temperature. An initial weight loss of about 5% at 50-130 °C due to the loss of water was recorded. This was followed by a steep transition at around 210 °C reflecting that the decomposition process involves a rapid loss in weight (around 61% at 500 °C). These results are also in a agreement with previous studies reported in literature^{14,15}. Also, two significant weight losses are observed in the TGA curve of chitosan–agar blended films. The weight loss data obtained from TGA for the pure components and their blends is summarized in Table 1. Some blends, such as the ratio 80/20, seem to be thermally enhanced. However, all the blended films show similar thermal stability to the pure components in general.

The continuous degradation observed in TGA curves of blended films (Figure 1) together with the absence of any phase separation confirms that chitosan and agar form highly compatible blends. This is highly associated with the interactions between agar and chitosan through hydrogen bonding formation between their functional groups ($-OH$ and $-NH_2$ groups in chitosan and $-OH$ groups in agar)¹⁶.

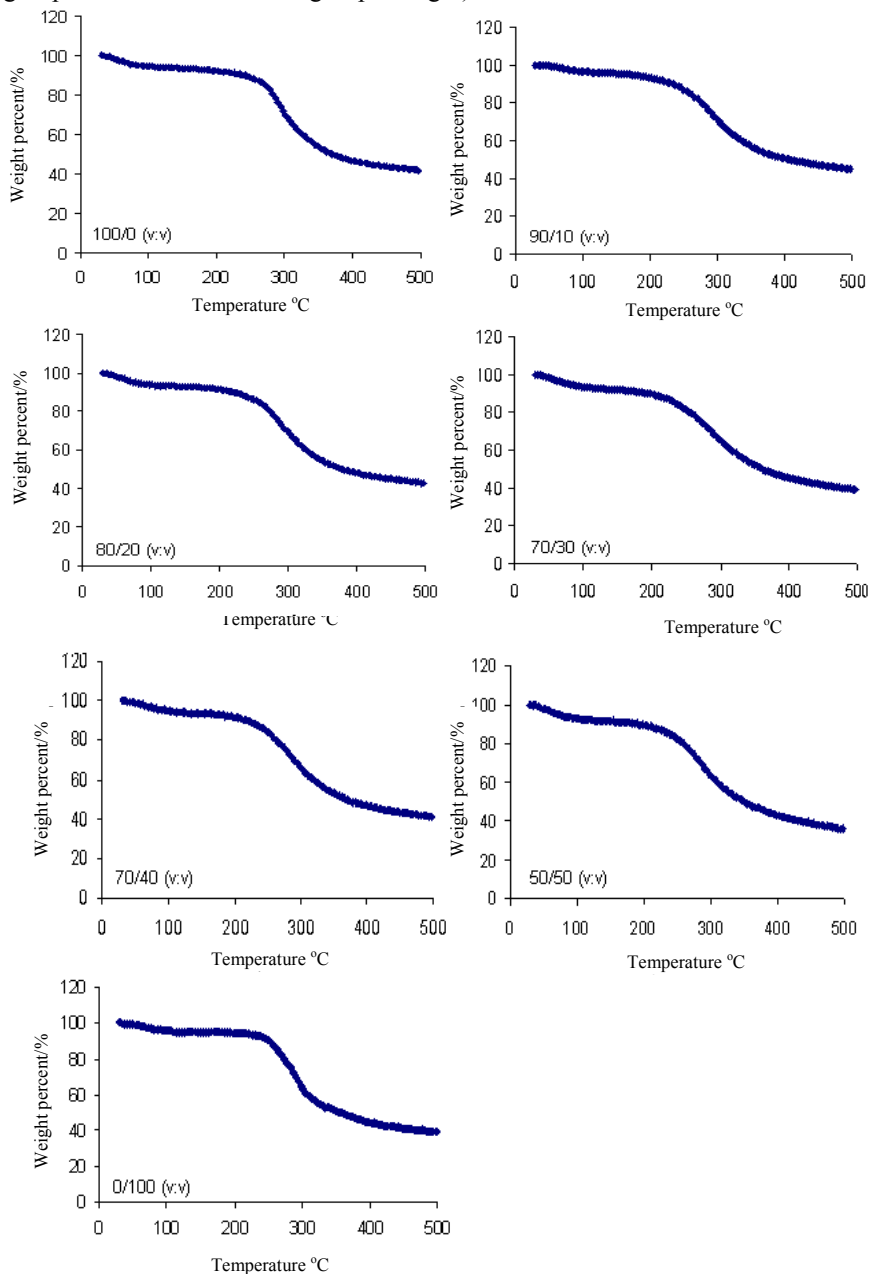


Figure 1. TGA curves of chitosan/agar blend films at various agar/chitosan proportions.

Tensile strength and elongation % at break

The variation of the tensile strength and the elongation % at break of the chitosan/agar blends films with different agar proportions are shown in Figure 2. It was found that pure chitosan film recorded the highest value of tensile strength *i.e.* 24.96 MPa as expected. As the amount of agar increased, the tensile strength decreased substantially until agar content reached 30% in the blend film wherein it remains almost constant. The elongation % dropped from 52.46% for pure chitosan film to 24.28% for 80/20 blend film after which it remains nearly constant with increasing agar content. This indicates that the blend films were more brittle than pure chitosan film. However, the reduction in both tensile strength and elongation% at break in the blend films is considered to be acceptable taking into consideration the nature of the two blended polysaccharides. The reduction in mechanical properties is most likely caused by the disruption in the crystallinity of chitosan accompanied the intermolecular interactions of agar with chitosan as agar content increases. However, the mechanical properties started to stabilize when more than 30% of agar was blended with chitosan suggesting possible crystalline structure dilution without considerable disruption in chitosan crystallinity.

Table 1. Weight loss (%) data of chitosan/agar blend film having various proportions at different temperatures of TGA runs.

Temperature, °C	Pure CS	90/10	80/20	70/30	60/40	50/50	Pure AG
100	5.7	6.5	3.6	6.7	5.3	7.4	4.4
200	7.9	8.7	6.9	10.6	8.5	10.7	5.5
300	30.4	31.8	29.7	35.5	34.8	37.6	37.1
400	53.5	52.2	49.6	54.8	53.5	57.4	55.6
500	58.3	57.2	55.1	61.0	59.0	64.4	60.8

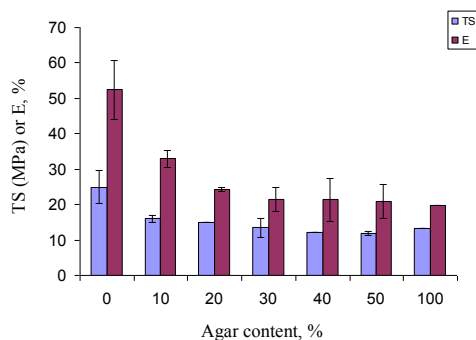


Figure 2. Tensile strength and elongation of chitosan and chitosan/agar blends.

Swelling behavior

Figure 3 shows the degree of swelling of pure and blend films versus the agar content. As can be seen all blended films showed higher degrees of swelling compared to pure chitosan film, indicating higher hydrophilicity. The degree of swelling for the blend films was found to be in the range of 386-457% while the degree of swelling for pure chitosan and pure agar

films was 89% and 620% respectively. This is because agar is a water-soluble polymer, which increases the water-uptake of chitosan when blended with chitosan due to the increase of the number hydrophilic groups (-OH) in the blends and high amorphous content. Similar behavior was reported for chitosan blended with the synthetic water-soluble polymer such as PVA^{17,18} in which the water uptake was similarly found to increase with PVA content.

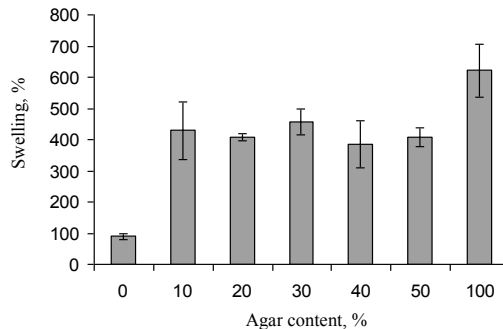


Figure 3. The degree of swelling of pure and blend films versus the agar content.

Contact angle measurements (surface hydrophilicity)

Figure 4 shows the relationship between the static water contact angle and the agar content for blended CS/AG films having various proportions. The plot shows that there is a general decrease in the static water contact angle with increasing the AG content in the blend *i.e.*, the surface becomes more hydrophilic when the concentration of AG increases in the blend. The contact angle of pure CS was $88.12^{\circ} \pm 1.91$, which is in agreement with the literature^{19,20} while the contact angle of the blended films ranged from 88.41 ± 2.90 to $72.03^{\circ} \pm 0.52$. In general, the contact angles for all blended films were less than 90° , indicating good hydrophilicity of the surfaces.

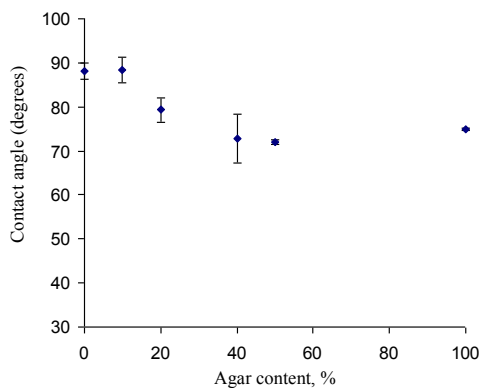


Figure 4. The relationship between the water-contact angle and the agar content for chitosan/agar blended films having various proportions (0% = pure CS and 100% = pure AG).

Conclusion

Blends of chitosan and agar in film forms were prepared at various proportions in the range of 90/10-50/50 (v:v). The obtained blended films possess hydrogel nature and can be

characterized by miscibility between chitosan and agar as confirmed by the results of TGA. Introducing agar to the blended films was found to enhance the thermal stability of some blended films under the influence of strong intermolecular hydrogen bonding existing between the amino groups of chitosan and the hydroxyl groups of agar. However, introducing agar to the blended films was found to decrease the tensile strength and elongation at break with increasing agar content. Studying the swelling behavior of the blend films showed that the water uptake was increased for all blend films compared to the pure chitosan film, indicating an enhancement in the hydrophilicity and gelation. The water contact angle measurements confirmed the increase in the hydrophilicity of the blended films with increasing agar content.

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