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Preparation and Characterization of Blend Films of Poly(Vinyl Alcohol) and Sodium Alginate

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Blend films of poly(vinyl alcohol) (PVA) and sodium alginate (NaAlg) were prepared by casting from aqueous solutions. This blend films were characterized by tensile strength test, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The miscibility in the blends of PVA and NaAlg was established on the basis of the thermal analysis results. DSC showed that the blends possessed single, composition-dependent glass transition temperatures (T_gs), indicating that the blends are miscible. FT-IR studies indicate that there is the intermolecular hydrogen bonding interactions, i.e. –OH…$^-$OOC– in PVA/NaAlg blends. The blend films also exhibited the higher thermal stability and their mechanical properties improved compared to those of homopolymers.

Keywords poly(vinyl alcohol), sodium alginate, blends, miscibility

Introduction

Alginates, a naturally occurring polysaccaride obtained from marine brown algae, comprising lineer chain of (1,4)-β-D-mannuronic acid and (1,3)-α-L-guluronic acid (1). Sodium alginate (NaAlg), a polyelectrolyte having rigid molecular chain (2), and good film forming ability, has been extensively exploited and studied in detail on biomedical applications as a drug carrier (3, 4).

Blending is an especially important process for developing industrial applications of polymeric materials. Compatibility among components has a marked influence on the mechanical properties of polymer blends (5). Intermolecular interactions regulate the compatibility among the component polymer molecules (5).

Blending, natural polymer with synthetic polymer seems to be an interesting way of polymeric composites. The selection and use of polymers can potentially form hydrogen bonds when two polymers mixed, as well as the study of blends properties, are of importance to find further applications of the resulting blend materials for biomedical and pharmaceutical devices. Cellulose was blended with poly(N-vinyl-2-pyrrolidone) (6), poly(methyl methacrylate) (7) and poly(2-hydroxy ethyl methacrylate) (8). Poly(vinyl alcohol) can be blended with poly(N-vinyl-2-pyrrolidone) (9) and hydroxypropyl methyl cellulose (10). Here, hydrogen bonding interaction is an important aspect of miscibility.

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NaAlg has some extent of rigidity and brittleness. For this reason, it is expected that mechanical properties of NaAlg can be improved through blending with poly(vinyl alcohol) (PVA) which is highly elastic feature and is also known as a biocompatible material. Accordingly, the blend of NaAlg and PVA is good candidate for new biomaterial with enhanced mechanical properties.

The objective of the present study is to prepare and characterize the NaAlg and PVA blend. We will report on the miscibility of the two polymers in the solid state due to inter-polymer interactions by means of mechanical measurements, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Experimental

Materials

Sodium alginate (high viscosity) and poly(vinyl alcohol) (MW = 72000 g/mol) were obtained from Sigma Chemical Co. and Aldrich, respectively and used as received.

Preparation of the Films

Aqueous solutions of the individual polymers (1% w/v) were mixed to obtain the desired proportions and stirred for 30 min at room temperature. The pure and mixture solutions both transparent (wt% of NaAlg; 9, 20, 33, 43, 50) were cast on petri dishes by water evaporation at 25°C. The films were dried under vacuum at 60°C for ten days. The dried films of thickness ranging 40 ± 7 μm were obtained.

Mechanical Measurements

The stress-strain measurements of the PVA, NaAlg and PVA/NaAlg blends were performed on an AG-I model mechanical testing apparatus (Schimadzu Co.) and a crosshead speed of 5 mm/min. The rectangular samples with dimensions at 25 mm × 10 mm × 40 ± 7 μm were analyzed at room temperature.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra of PVA, NaAlg and PVA/NaAlg blends were measured on a Nicolet 520 FT-IR spectrophotometer using KBr (potassium bromide) pellet technique.

Thermogravimetric Analysis (TGA)

The dynamic weight loss experiments of PVA, NaAlg and PVA/NaAlg blends were carried out on a TA instrument 2050 thermogravimetric analyzer (TGA). All tests were conducted in a N_2 purge (25 mL/min) using sample weights of 5–10 mg over a temperature range 25°C to 700°C at a scan rate of 10°C/min.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures of the PVA, NaAlg and PVA/NaAlg blends were determined by use of a TA instrument DSC 2010 thermal analyzer system. All samples were tested in crimped aluminum pans at a heating rate of 10°C/min under dry N_2 gas (25 mL/min) over a temperature range from 20°C to 170°C. The glass transition temperatures were determined as the average at least three separate measurements.

Results and Discussion

In the course of studying PVA/NaAlg blends, we have found that NaAlg forms optically clear homogeneous blends with PVA and that the Young modulus and the tensile stress of the blends are greater than the homopolymers. The results of the stress-strain measurements of PVA, NaAlg and PVA/NaAlg blend films were presented in Figure 1. NaAlg showed a tensile strength of 33 MPa and elongation at break of 6.5%. Upon mixing with PVA, both the tensile stength and elongation at break generally increased with increasing NaAlg content. This appearance suggests the existence of specific intermolecular interaction between NaAlg and PVA, such as those reported for the blend films of silk fibroin/NaAlg (11) and poly(acrylamide)/NaAlg (12) (Figure 2).

FT-IR spectroscopy is one of the most powerful techniques for investigation of multi-component system, because it provides information on the blend composition as well as on the polymer-polymer interaction. Our discussion will mainly concentrate on the hydroxyl and carbonyl stretching vibration bands in Figure 3, as expected to be affected by hydrogen bonding interactions.

Figure 3 shows the FT-IR spectra for PVA, blends and NaAlg samples. The bands of NaAlg appeared at 3500 cm^{-1} for the hydroxyl groups and at 1613 and 1415 cm^{-1} for the asymmetric $-COO^-$ stretching vibration and symmetric $-COO^-$ stretching vibration, respectively. The spectrum of the PVA/NaAlg blend films was characterized by the presence of the absorption bands typical of the pure components, with the intensity roughly proportional the blending ratio. The characteristic band of NaAlg appeared at 1613 cm^{-1} was observed in all the spectra of the blends and the band shifted to a lower frequency range, indicating that there should occur a stronger hydrogen bonding

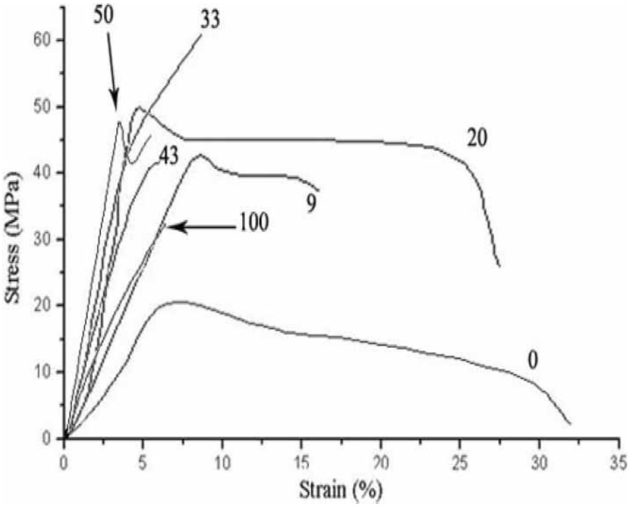


Figure 1. Stress-strain curves of the pure and blend films.

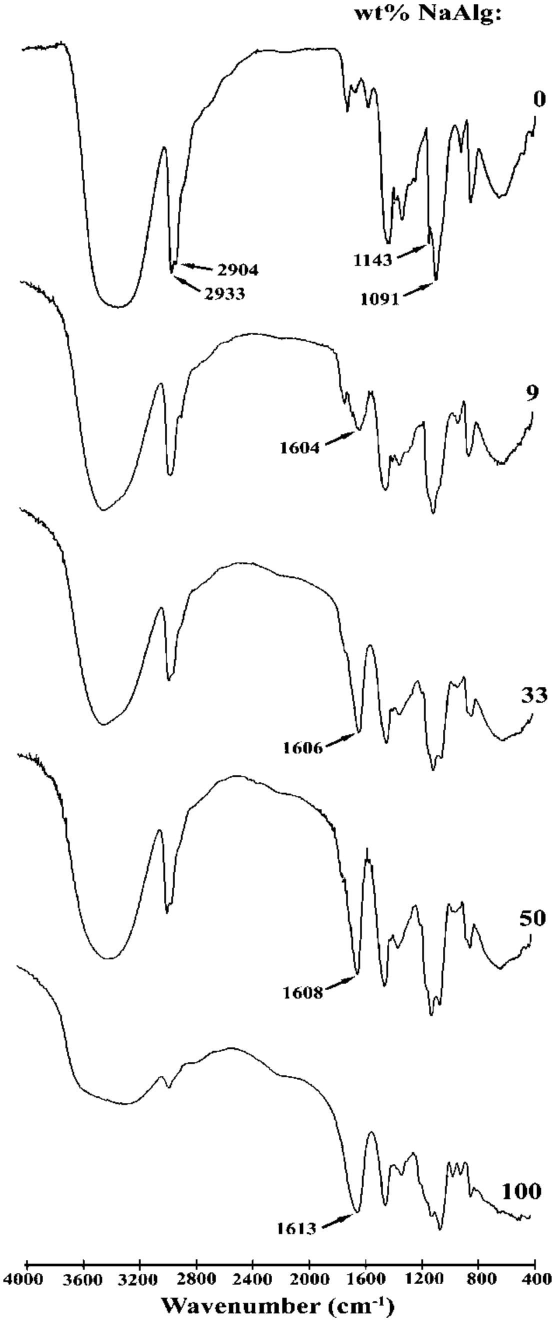


Figure 2. The FT-IR spectra of the pure and blend films (4000–400 cm^{-1}).

interaction between –OH of PVA and –OH or –COO$^-$ of NaAlg in the blend. In addition, it is noticed that the hydroxyl stretching bands became much broader with increasing NaAlg content. This also strongly supports the idea that a hydrogen bonding can form between –OH of PVA and –OH or –COO$^-$ of NaAlg (Scheme 1).

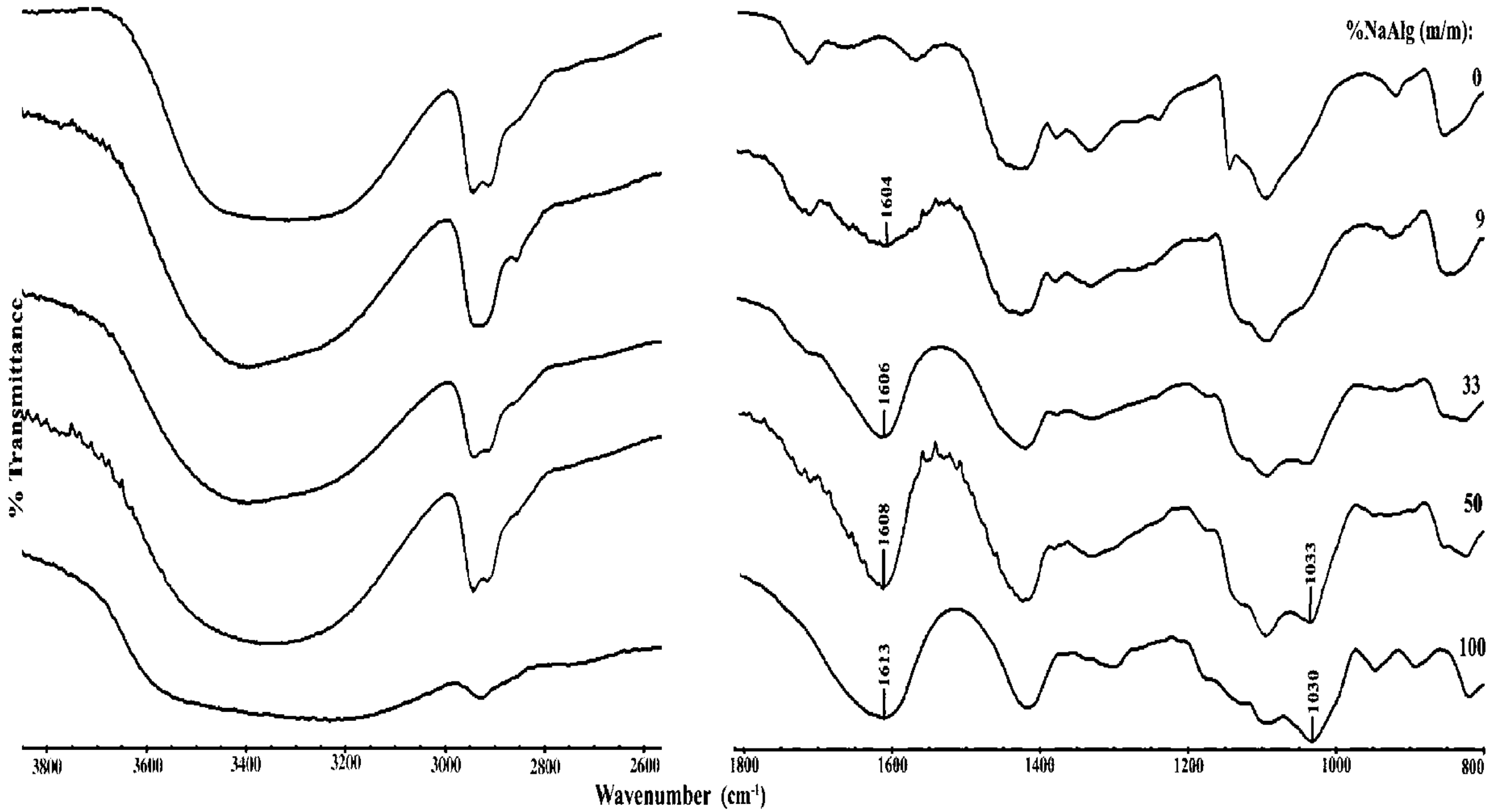
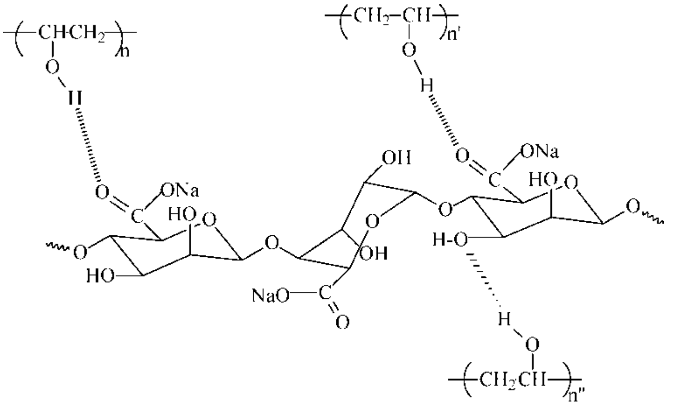


Figure 3. The FT-IR spectra of the pure and blend films (3900–2500 cm^{-1} and 1800–800 cm^{-1}).



Scheme 1.

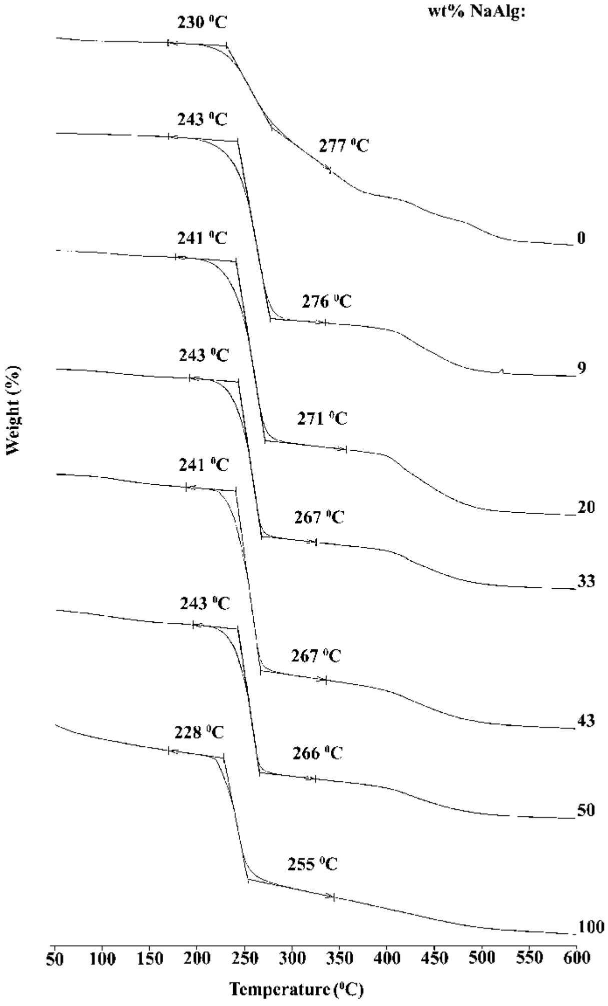


Figure 4. The TGA curves of the pure and blend films.

Typical weight loss (TG) and derivative of weight loss (DTG) curves of PVA, NaAlg and PVA/NaAlg blends were presented in Figures 4 and 5. From the TG curves initial degradation temperature and final degradation temperature were determined. From DTG curves, the maximum temperatures of weight loss were also noted.

The mass loss of pure PVA begins at 230°C and reaches to maximum at 254°C. However, the mass loss of pure NaAlg starts at 229°C and reach to maximum at 243°C. The PVA and NaAlg have almost the same thermal stability. The TG curves of both NaAlg and PVA also indicate one reaction stage which is reflected as single peak in the DTG curves (Figure 5). Similarly, PVA/NaAlg blends degrade in one step due to the thermal degradation temperature of the components rather close to each other. This is evidenced by the appearance of only one degradation reaction peak in DTG thermograms.

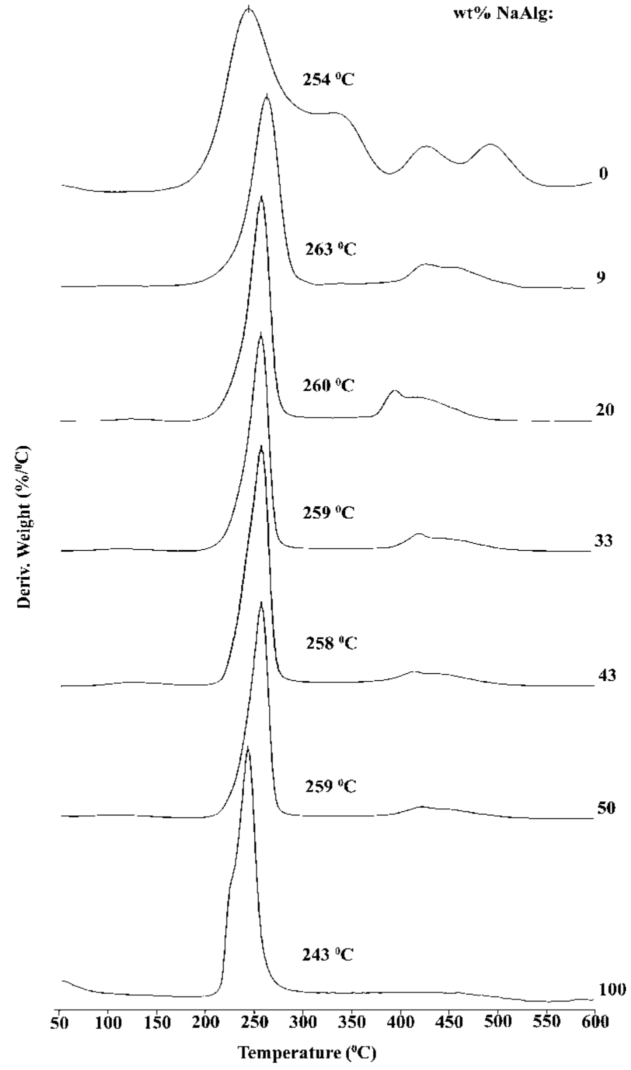


Figure 5. The DTGA curves of the pure and blend films.

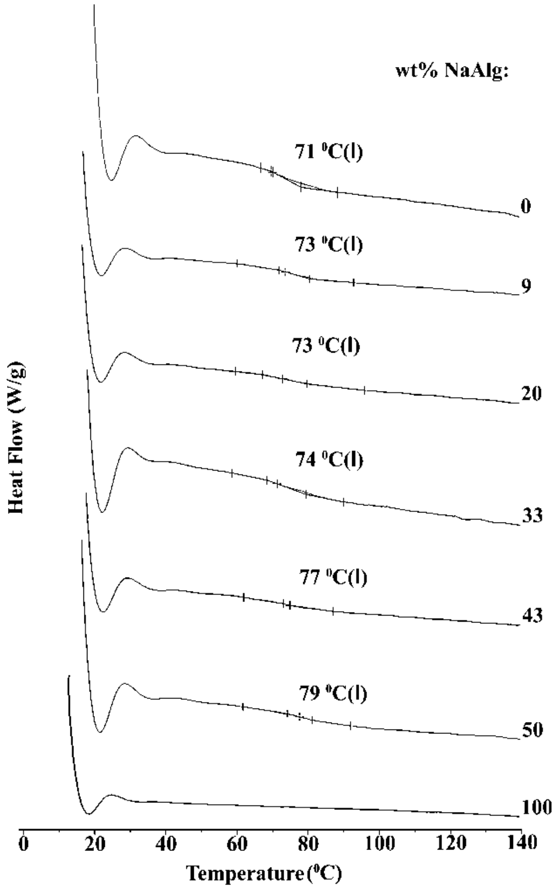


Figure 6. The DSC curves of the pure and blend films.

However, the initial thermal degradation temperature of the blends is greater than the homopolymers which indicates that there is a specific intermolecular interaction between NaAlg and PVA in the PVA/NaAlg blends.

DSC curves of PVA, NaAlg and PVA/NaAlg blends were illustrated in Figure 6. The observed glass transition temperatures (T_g) are depicted by arrows in this figure. It is well known that miscible blends show a single T_g intermediate to those of the pure components. For pure PVA and all PVA/NaAlg blends, a single T_g value is clearly observed, and the each observed T_g depends on the blend composition (Figure 6). This suggests that the blends are miscible for all composition. On the other hand, in the same figure it was difficult to detect the T_g of the pure NaAlg. However, it can be seen that the T_g is low for PVA homopolymer ($T_g = 71°C$) when compare with that of the PVA/NaAlg blends. However, the T_g for these blends were slightly increased from 72°C to 79°C with the increase of NaAlg content in the blend. This behavior was also attributed to the hydrogen bonding formation between PVA and NaAlg units of these blends. Because, the mobility of the chains decreases due to the presence of hydrogen bonds that acts as crosslinks.

Acknowledgements

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