The Preparation and Characterization of Chitosan / Poly (Vinyl Alcohol) Blended Films

ESAM A. EL-HEFIAN*, MOHAMED MAHMOUD NASEF[§] and
ABDUL HAMID YAHAYA

Department of Chemistry, Faculty of Science,
University of Malaya, 50603 Kuala Lumpur, Malaysia.

[§]Chemical Engineering Department, Faculty of Chemical and Natural Resources
Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

eelhefian@yahoo.com

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Abstract: In this study, chitosan and PVA were blended at different proportions (considering chitosan as the main component) in solution forms. The chemical structure and the morphology of the obtained blend films were investigated using FTIR and field emission scanning electron microscope (FESEM). The thermal stability of the blend films were also studied using thermal gravimetric analysis (TGA). Our results showed that chitosan and PVA form a compatible blend and their films displayed homogenous and smooth surface properties compared to their individual pure components. The blending of PVA with chitosan at all proportions was found to highly enhance the swelling of the obtained films compared to that of pure chitosan one.

Keywords: Chitosan, Poly (Vinyl alcohol), Blending, Films.

Introduction

Chitosan is a natural polysaccharide formed by alkaline deacetylation of the second most abundant naturally occurring chitin of crab and shrimp shells¹. Due to the amino groups that chitosan possesses in its chain, it 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 evaluated for numerous applications, including medicine, food, cosmetics and wastewater treatment²⁻⁶.

Poly (vinyl alcohol) is a non-toxic, water-soluble synthetic polymer that has good film-forming ability. It has a large number of hydroxyl groups which allows it to react with many types of functional groups. This advantage makes it suitable for biocompatible materials. PVA has been widely used on biomaterial applications⁷.

To improve chitosan properties and further diversify its applications, various strategies have been adopted. This includes: (1) crosslinking⁸ (2) graft copolymerization^{9,10}, (3) complexation¹¹, (4) chemical modifications¹² and (5) blending^{13,14}. In particular, the modification of chitosan by means of blending is an attractive method that has been extensively used for providing new desirable characters to chitosan^{15,16}. This is mainly due to its simplicity, availability of wide range of synthetic and natural polymers for blending and effectiveness for practical utilization.

In this work, we report on the preparation of chitosan/poly (vinyl alcohol) films obtained by the physical solution blending of chitosan and PVA at different proportions. FTIR spectral analysis was used to confirm the presence of functional groups of both chitosan and PVA in the blend. The properties of various blended films of CS/PVA, such as swelling, thermal stability and morphology were also investigated.

Experimental

Chitosan with a degree of deacetylation (DD) of 88.1% determined by UV method¹⁷ was purchased from a commercial source. PVA Fluka (56-98) with an average molecular weight of $195 \times 10^3 \text{ g mol}^{-1}$ was also used in this work. Acetic acid (glacial 100%, pro-analysis) was purchased from Merck (Darmstadt, Germany). Ultra pure water (Maxima Ultra Pure Water, Elga-Prima Corp, UK) with a resistivity greater than $18 \text{ M}\Omega/\text{cm}$ was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were used in all experiments.

Preparation of the solutions

The 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 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 PVA was prepared by dissolving 5 g of PVA in 500 mL of preheated ultra pure water. The solution was then stirred and kept at about 90°C for 2 h.

Preparation of the blended films

The preparation of blended films of chitosan and PVA was carried out at various proportions. The aqueous PVA solution was added drop by drop to the chitosan solution, under continuous stirring at around 94°C . Stirring was allowed to continue for 30 min after mixing and the range of the added PVA to chitosan solution was from 0-50 vol%. Films of the resulting homogeneous solutions were obtained by casting prescribed amounts of the solutions onto polystyrene petri dishes followed by drying at 60°C for 48 h. The films were peeled off and kept under evacuated desiccator over fresh silica gel until use. All films obtained were transparent and free of air bubbles.

Similar films from pure chitosan and pure PVA were prepared using the same casting procedure and used as references. The chitosan films were neutralized with 0.1 M NaOH solution overnight washed thoroughly with distilled water and dried subsequently.

Film thickness

The film thickness was measured with a digital micrometer (Mitutoyo, Japan) with 0.001mm resolution. Several thickness measurements were taken at several points of the film and then, the average was calculated.

Instrumentation

Molecular weight measurements

The molecular weight of chitosan was about $5.5 \times 10^5 \text{ g mol}^{-1}$ 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 $\times$ 7.5 mm) and the solvent used was 1% acetic acid. The GPC was calibrated using pullulans as standard.

FTIR measurements

FTIR measurements of blended films (about 10 μm thick) were performed on a spectrometer (Perkin Elmer, model 2000). The spectra were obtained at a frequency range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and 8-times scanning.

FESEM measurements

The surface morphology was investigated by a FEI Quanta 200F field emission scanning electron microscope (FESEM) (FEI, USA) controlled by a 32 bit computer system using Microsoft Windows 2000 as an operating system.

Thermogravimetric measurements

TGA was used to evaluate the thermal stability and to determine the decomposition temperature of chitosan. Thermogravimetric measurements were performed using a Mettler-Toledo thermogravimetric analyzer model TGA/SDTA851e. TGA runs were carried out in a temperature range of 30-500 °C, under nitrogen atmosphere and with a constant heating rate of 10 °C/min in all the experiments. The sample size of 4-10 mg was weighed and the mass of the sample pan was continuously recorded as a function of temperature.

Degree of swelling

The swelling behavior of the films was measured by immersing the blended films in distilled water at room temperature for 10 h. The excess water on the surface of the films was removed by blotting the surface with 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 is the weight of completely dried sample and W_2 is the weight of swelled sample.

Results and Discussion

FTIR analysis of pure CS and pure PVA films

As shown in Figure 1, the spectrum of pure chitosan film shows a broad band at 3367 cm^{-1} which is due to the OH stretching. The band at 1560 cm^{-1} is assigned for the NH bending (amide II) (NH_2) while the small peak at 1647 cm^{-1} is attributed to the C=O stretching (amide I) O=C-NHR. The bands at 2927, 2884, 1411, 1321 and 1260 cm^{-1} are assigned to CH_2 bending due to pyranose ring¹⁸. The band at 1380 cm^{-1} is due to CH_3 wagging. The characteristic features of chitosan spectrum in this study are similar to that of previous reports¹⁹⁻²¹. Figure 1 also presents the FTIR spectrum of the pure PVA film. The spectrum shows an absorption peak at 3368 cm^{-1} which refers to the intermolecular hydrogen bonding and -OH stretch vibration²². The vibrational band observed at 2941 cm^{-1} is associated with the C-H stretching from alkyl groups. The absorption corresponding to the -C-O stretching occurs at 1096 cm^{-1} .

FTIR Analysis of CS/PVA blended films

Figure 1 shows the FTIR spectra of chitosan and PVA blended films containing various PVA proportions. A summary of characteristic bands of chitosan and PVA blended films is also presented in Table 1. As can be seen, the increase in the PVA concentration in the blended films caused a decrease in the intensity of the band arising from the NH bending (amide II) at 1561 cm^{-1} of chitosan. Also, an increase in the intensity of CH group at around 2928 cm^{-1} was observed as the PVA content increases. In addition, there was a remarkable shift for the peak at 1077 cm^{-1} to a higher wave number with the increase of PVA content in the blend. Furthermore, the band at 850 cm^{-1} disappeared in the spectra of the pure chitosan film and the chitosan/PVA blend film containing PVA concentration of 10%.

Figure 1. Typical FTIR spectra of pure chitosan, pure PVA and their blended films having various proportions

Table 1. FTIR characteristic bands of chitosan/PVA blend films

CS/PVA, %	C-C	C-O	C-O stretch	CH	NH amide II	C=O amide I	CH	OH
100/0	-	1033	1077	1380	1561	1648	2928	3368
90/10	-	1035	1077	1386	1559	1647	2927	3367
80/20	850	1035	1078	1379	1559	1647	2935	3367
70/30	851	1036	1079	1379	1559	1647	2937	3367
60/40	850	1039	1082	1380	1559	1647	2939	3367
50/50	851	1037	1087	1379	1559	1647	2940	3367
0/100	852	-	1094	1375	-	-	2941	3368

However, the intensity of this band was increasing for the other ratios as the content of PVA increased. This is due to the fact that when two or more polymers are mixed, changes in characteristic spectra peaks occur due to the reflection of the physical blends and chemical interactions^{23,24}. These observations indicate the existence of good miscibility between chitosan and PVA and this is most likely due to the formation of intermolecular hydrogen bonds between the amino and hydroxyl groups in chitosan and the hydroxyl groups in PVA.

FESEM measurements of CS/PVA blended films

Figure 2 shows the SEM micrographs of surfaces of chitosan/PVA blended films containing different proportions of PVA together with the corresponding ones of pure chitosan and PVA films. As can be seen, chitosan film shows smooth and homogeneous surface with some straps unlike that of pure PVA where no straps are seen. The surfaces of the blended films of chitosan and PVA are homogeneous with no pores²⁵ and have no interface layer. The blended films also exhibit flat smooth surface in general indicates the uniform distribution of CS and PVA molecules throughout the films. The formation of homogeneous blends of chitosan and PVA was mostly caused by the interactions of hydrogen bonds between the functional groups of the blended component ($-OH$ and $-NH_2$ groups in chitosan and $-OH$ groups in PVA).

Figure 2. The scanning electron micrographs of pure CS film, pure PVA film and CS/PVA blend films; (a) pure CS, (b) pure PVA, (c) 90/10, (d) 80/20, (e) 70/30, (f) 60/40 and (g) 50/50

TGA of pure chitosan film, pure PVA film and their blended films

The representative TGA curves for the pure CS, pure PVA and CS/PVA blended films are shown in Figure 3. A two-stage weight loss was recorded for the chitosan film. The first transition falls in the range of 40 °C -130 °C and shows about 6% loss in weight. This is due to the moisture vaporization inside the film. The second weight loss begins at about 150 °C and the corresponding weight loss of about 52%, is attributed to the decomposition of chitosan. The total weight loss of the sample at about 500 °C is 58%. Similar behavior of chitosan film was reported in the literature²⁶⁻²⁸.

Figure 3. TGA thermograms of pure CS film, pure PVA film and their blended films having various proportions

As it can be seen, the pure PVA film exhibits a three-step degradation pattern. The first step began around 40 °C up to 79 °C with a weight loss up to 3%. The second and the major mass loss is between around 260 °C to 430 °C with a weight loss of about 73%. This was followed by a further smaller mass loss (around 17%) in the third step (from about 430 °C to 480 °C). The first step of weight loss could be attributed to the evaporation of loosely bound water. The second step is predominantly caused by the heat decomposition of the polymer structure. With further heating, the polymer backbone is broken down. Similar observations have been reported in literature^{29,30}.

The weight loss data obtained from TGA for pure components and their blends are summarized in Table 2. It can be clearly seen that the blended film having CS/PVA ratio of 50/50 shows the lowest amount of water content unlike blended films containing other ratios which show higher water content compared to pure chitosan film. A closer examination of Figure 3 reveals that all blends have only one onset (the degradation start temperature) suggesting that interaction may exist between the two components in each blend³¹ due to the formation of hydrogen bonding between the functional groups of the blended components ($-\text{OH}$ and $-\text{NH}_2$ groups in chitosan and $-\text{OH}$ groups in PVA).

Table 2. The weight loss (%) of the pure components and their blends at different temperatures

Temperature, °C	Pure CS	90/10	80/20	70/30	60/40	50/50	Pure PVA
100	5.7	6.1	6.9	6.3	6.2	3.9	3.1
200	7.9	8.7	10.3	11.5	12.3	7.0	3.1
300	30.4	32.7	35.6	39.0	38.7	31.0	7.1
400	53.5	56.6	60.9	69.7	77.2	65.6	68.6
500	58.3	61.3	67.1	76.8	86.3	74.9	92.8

Swelling behavior

In this work as shown in Figure 4, all the blended films showed much higher degree of swelling comparing with the pure chitosan film, indicating their higher hydrophilicity. The degree of swelling for the blended films ranging from 1047% to 2117% while the degree of swelling for pure chitosan and pure PVA films were 89% and 674% respectively, which indicates that the swelling behavior is greatly influenced by the PVA content in the blend. This is because PVA is a water-soluble polymer and the blending of chitosan with PVA tends to increase the water uptake due to the increasing of hydrophilic groups ($-\text{OH}$) in the blends. Also, the PVA chains are physically entangled with the chitosan chains leading to the formation of a hydrogel network³². It was reported that the blending of chitosan with the PVA^{33,34} leads to an increase in the water uptake with increasing PVA content.

Figure 4. The swelling degree of chitosan, PVA and their blended films

Conclusion

Blended films of chitosan and PVA were prepared at various proportions. Investigation of the properties of the obtained blends displayed good miscibility between chitosan and PVA as revealed by the results of FTIR, FESEM and TGA due to the strong intermolecular hydrogen bonding existing between the amino groups of chitosan and the hydroxyl groups of PVA. Studying the swelling behavior showed much higher water uptake for all blended films compared to that of the pure chitosan film, indicating an enhancement in the hydrophilicity.

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