



Production of Novel Composite Films Based on PVA-Biosilica

E.C. Kılıç^(a), E. Akyol^(a), B. Karakuzu İkizler^(b), A.C. Özarslan^(b), C. Özel^(b), S. Yücel^(b)

^a Department of Chemical Engineering, Yıldız Technical University, Istanbul, Turkey

^b Department of Bioengineering, Yıldız Technical University, Istanbul, Turkey

*E-mail: yuce.sevil@gmail.com

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In this study, PVA/silica gel composite films were prepared. For this, sodium silicate solution was produced from rice hull ash (RHA) which is a cheap agricultural waste by alkali extraction method. Sodium silicate solutions were gelled at pH 7 with HCl addition by sol-gel method. Silica gels were added to PVA films at first time with this study to make films which is different than the literature studies. Composite films were produced by using obtained gels and PVA with three different viscosity grades. PVA, has different viscosity and same hydrolysis degrees; 5:88, 26:88 and 40:88. PVA/silica gel films were obtained by drying at room temperature for 24 hours and in vacuum. Structural characteristics of prepared PVA/silica gel films were determined by FT-IR analysis and their surface morphology was determined by SEM. Films obtained with high viscosity PVA showed homogeneous structure and slightly higher water absorption capacity.

Keywords: PVA films, sodium silicate solution, sol-gel method, water absorption.

Introduction

Poly(vinyl alcohol) (PVA) films have been commonly used in glucose sensors, immuno-isolation membranes, contact lenses and drug delivery systems applications due to its biocompatible, inherent non-toxicity, and good filming formation properties¹⁻⁴. These properties make it suitable for many packaging applications⁵. However, it has low mechanical properties and water resistance⁶⁻⁷. To overcome this drawback, it is essential to reinforce with applicable nanofillers to improve their mechanical and barrier properties⁸. Recent studies have shown that the introduction of additives like titanium dioxide, and silica into polymeric materials can be used to enhance mechanical properties and water resistance of PVA films⁹⁻¹¹. Ismail et al. (2014) and Tang et al. (2008) reported positive effect of silica content (SiO₂) on mechanical properties and water resistance of PVA films. SiO₂ has good compatibility with PVA due to the formation of Si-O-C chemical bond at the

interface between SiO₂ and PVA leading to good dispersion of silica in the PVA matrix¹²⁻¹³. Although, many studies indicated that filler can improve the performance of polymer materials such as plastic and rubber, there have been very few relevant studies regarding PVA polymers modified by silica¹⁴. In this study, we successfully prepared PVA/silica gel composite by using silica gel obtained by sol-gel technique from the rice husk ash, which is agricultural waste, as a source of silica¹⁵. The evaluation of biosilica from rice husk ash not only helped to decrease the fabrication costs but also lower the environmental pollution.

Experimental

Preparation of Silica Gel

Sodium silicate solution was prepared by alkaline extraction of RHA according to previous studies¹⁶. Briefly, rice hull ash was burned at 600 °C in muffle furnace for 5 hours. The obtained ash was added in distilled water and pH of the solution was decreased to 1 with hydrogen chloride (HCl). The solution was

boiled for 1 hour. Acid leached ash was mixed with sodium hydroxide (NaOH) for 1 hour. Thus, sodium silicate solution was obtained. After, strong acid, HCl, was added in sodium silicate solution until reaching gelation. Obtained silica gel was aged for 24 h. Then washed and centrifuged three times to remove sodium before production of composite films.

Composite Film Production

The washed silica gels was mixed for 4 h with a mass ratio of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 in 5% PVA solutions which have different viscosity and same hydrolysis degrees; 5:88, 26:88, 40:88; (PVA:Silica gel; wt:wt (%); respectively). Films are obtained successfully with all 90:10, 80:20 and 70:30 mass ratios. However, films with 60:40 and 50:50 mass ratios are obtained successfully with only 40:88 PVA. So, the results are given for 3 different viscosity degrees with 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90 PVA:Silica gel ratio. To ensure the homogeneity, mixtures were blended with using homogenizator for a while. Then 3 ml of homogeneous samples were poured into petri dishes. After, the samples were dried with two different drying processes, for two days at room temperature or for 9 h at 40 °C in a vacuum oven.

Characterization of Composite Films

The chemical functional groups of composite films were evaluated by FT-IR (Fourier Transmission Infrared) Spectroscopy with an ATR (attenuated total reflection) unit in the range of 4000 cm^{-1} –650 cm^{-1} . Data were collected in transmittance mode. Morphological structure of composite films was studied using SEM (Scanning Electron Microscopy). All samples were coated with gold prior to the SEM analysis by using a Sputter Coater device. For water absorption studies, initial weight (W_i) of all samples were measured and the mass changes, e.g. wet weight (W_w) and dry weight (W_d) were determined for various time periods (for first 30 minute, each 5 minutes and then 1, 2, 3, 5, 10, 24, 48, 72;

hour). The water absorption capacity (W_A) (Eq. 1) was calculated as¹⁷;

$$W_A\% = \frac{(W_w - W_d)}{W_d} \times 100 \quad (\text{Eq. 1})$$

Results and discussion

Table 1 shows film forming success of PVA- silica gel composites with different PVA.

Table 1. PVA/Silica Gel Films with Different Viscosity Values

PVA/Silica gel (Weight Ratio)	5:88 PVA	26:88 PVA	40:88 PVA
90:10	√	√	√
80:20	√	√	√
70:30	√	√	√
60:40	X	X	√
50:50	X	X	√
40:60	X	X	X
30:70	X	X	X
20:80	X	X	X
10:90	X	X	X

(√: film formed, X: film not formed)

Characterization Results

Chemical Functional Group Determination of Composite Films

The FT-IR spectra obtained from all composite films were given in Fig. 1 and Fig.2. The results show that the polyvinyl alcohol/silica gel composite film was successfully synthesized.

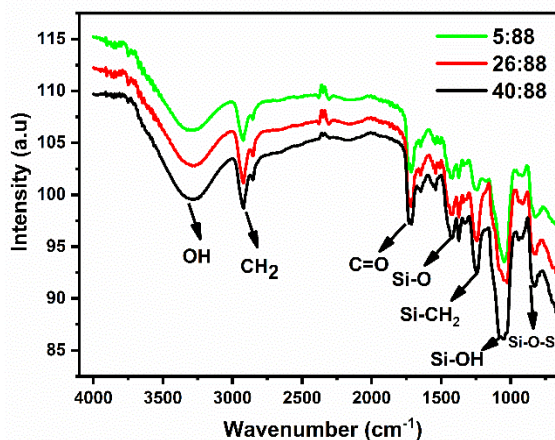


Fig.1. FT-IR spectra of 90:10 ratio PVA-5:88/silica gel, PVA-26:88/silica gel, PVA-40:88/silica gel structures

In the spectra, Si-O groups are absent at 1420-1470 cm^{-1} wavenumber, the broad band at 1000-1100 cm^{-1} arose from Si-OH groups and 800-900 cm^{-1} arose from Si-O-Si groups. Additionally, asymmetric and symmetric $-\text{CH}$, $-\text{CH}_2$ bands and C=O stretching are seen at 2800-2900 cm^{-1} and 1700-1750 cm^{-1} respectively. The broad band at 3350-3450 cm^{-1} arose from $-\text{OH}$ groups, which were originated from PVA. Other Si-CH₂ band, which is at 1200-1250 cm^{-1} , indicates PVA-silica composite structure.

When the FT-IR spectra of the PVA-5:88/Silica, PVA-26:88/Silica, PVA-40:88/Silica gel composites with 90:10 ratio are examined, the Si-CH₂ peaks which shows the composite formation are more intense especially for 26:88 and 40:88 (Fig.1).

In Figure 2, FT-IR spectra of PVA-40:88 /Silica gel structures in different ratios (90:10, 80:20, 70:30, 60:40, 50:50) are given. In the spectrum of the PVA/silica-gel with 90:10 ratio, it is seen that the Si-CH₂ group separates from the Si-OH group and appears as a clear peak. In other films, the dense Si-OH group is seen more clearly.

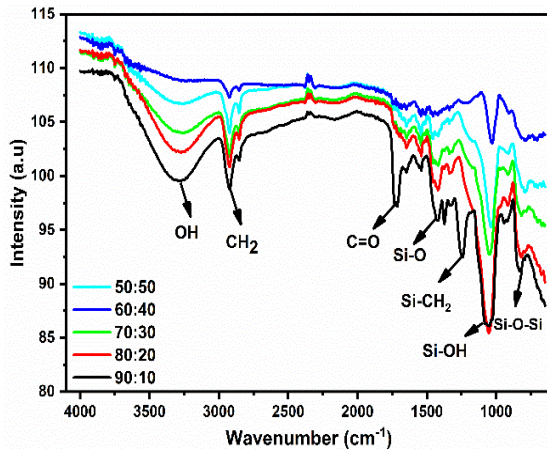


Fig.2. FT-IR spectra of PVA-40: 88 / Silica gel structures in different ratios (90:10, 80:20, 70:30, 60:40, 50:50)

The Morphology of Composite Films

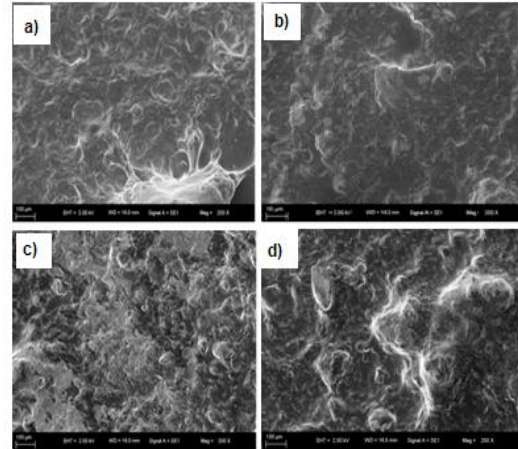


Fig.3. SEM Images of PVA-Silica Gel Films (a) PVA-5:88/silica gel (b) PVA-26:88/silica gel (c) PVA-40:88/silica gel composite dried at room temperature (d) PVA-40:88/silica gel composite dried under vacuum

Surface morphology of the composite films were examined using scanning electron microscopy (Fig.3). Since the most homogeneous distribution is seen in 90:10 ratio of PVA silica-gel composite films, SEM analysis were made only for this sample. According to SEM images, silica particles are seen clearly in low and medium viscosity of PVA films. This may indicate that physical bonding is weaker than high viscosity PVA films. Fig.3 (d) shows the SEM images of PVA-40: 88/Silica gel obtained by drying under vacuum at 40 °C. In Fig.3 (c) , it is understood that PVA-40: 88/ Silica gels dried under room conditions have a more homogeneous film appearance. In films dried under vacuum, it is understood from the dense appearance of silica particles on the surface that the bonding between silica and PVA is weaker.

Water Absorption Capacity Investigation of Composite Films

The water absorption capacity and the degradability are the most important properties for biodegradable materials¹⁸. At certain times during the first 30 minutes and 72-hours period, water absorption (percentage) (Fig. 4 and Fig. 5) were calculated by the mass change of composite films. Each composite films (size: 1cm×1cm) were immersed in 30 mL of distilled water and absorption studies were performed at two different conditions, in an oven at 40 °C or room temperature.

Effect of PVA/SiO₂ Weight Ratios on Water Absorption Properties of Produced Films

Effect of PVA/SiO₂ weight ratios on water absorption properties of produced films was given in Fig.4.

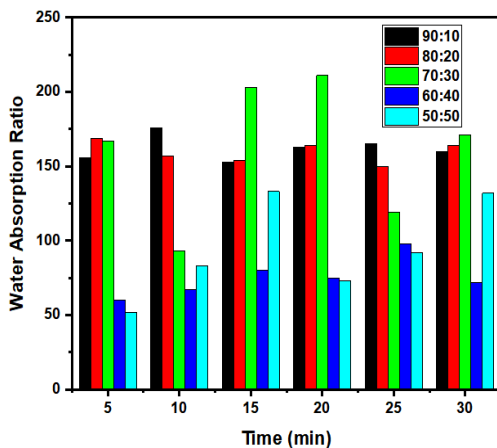


Fig.4. Water Absorption of Films Produced with 40:88 PVA (first 30 minutes)

The films in the ratio of 90:10 showed 156% swelling after the first 5 minutes after immersion in water and the values taken during the first 30 minutes remained close to this rate. Likewise, the 80:20 film swelled 169% after the first 5 minutes after being placed in water and the values taken during the first 30 minutes remained close to this rate. There was an increase at beginning and then decrease in the swelling rates of the 70:30 film in the first 30 minutes. It was observed that it swelled at a high rate at the

20th minute, but there was a decrease in the swelling values after the 25th minute. The films in the ratio of 60:40 and 50:50 showed very low water absorption compared to other films. The 50:50 film showed swelling by absorbing a high rate of water in the 15th and 30th minutes.

In Figure 5, the first 72 hours water adsorption graph and values of the films in the ratio of 90:10, 80:20, 70:30, 60:40 and 50:50 kept at room temperature are given. The 90:10 ratio film showed 285% swelling after the first hour, and this ratio remained the same until the end of the 72nd hour. The swelling ratios of 80:20 film showed more pronounced ups and downs than 90:10 film. There was an increase in the swelling rates at the 10th hour, but it was seen that the swelling rate was reduced again at the 24th hour. There were ups and downs in the swelling ratios of the 70:30 film as in the 80:20 ratio. Especially in the ratios of 70:30 and 80:20, the highest swelling rates were found at the 10th hour, which reached high values such as 300% and 361%. Decreases were seen after the 10th hour. Films in the ratio of 60:40 and 50:50 have the lowest swelling rates. The swelling values (about 60%) of the 60:40 film at the end of the first 5 minutes and 1 hour is close to each other. For 50:50 film, swelling values decreased much at the end of 1 hour.

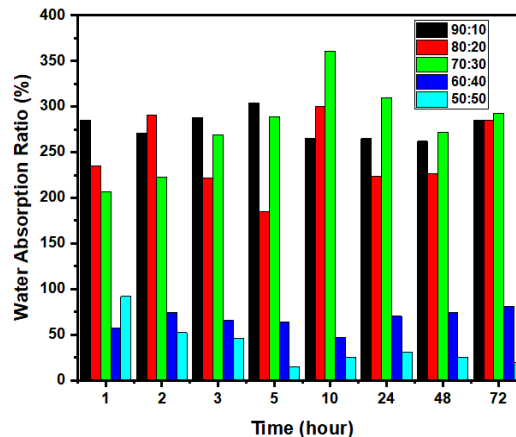


Fig.5. Water Absorption of Films Produced with 40:88 PVA (72 hours) at room temperature

If we generalize, increasing of silica gel in composite films caused less water absorption. While the PVA: silica- gel ratio changed between 90:10-50:50, absorption values of 40:88 PVA/silica gel film changed between 285-19 % after 72 hours. This is because of the network structure formed by combining silica with PVA plastic films, which improved the water resistance and prevented the water molecules from dissolving the films.

The Effect of Viscosity PVA on Film Properties

The viscosity of PVA affected the water absorption capacity of composite films. With the increase of PVA viscosity in composite films, water absorption capacity decreased. The lowest water absorption values were obtained with 40:88 PVA

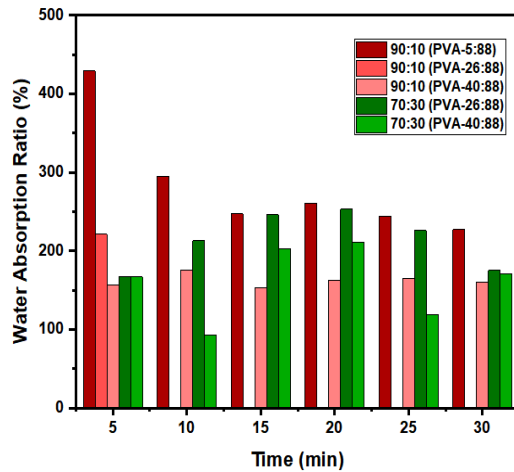


Fig.6. The Effect of Viscosity PVA on Film Properties (70:30 and 90:10)

Effect of Different Drying Conditions on Water Absorption Properties of Produced Films

Fig.7 is showing the Water Absorption of Films Produced with 40:88 PVA at 40 °C. It was observed that the ambient temperature significantly affects water absorption values. For all films dried and kept at ambient temperature, the swelling values (at 40 °C) were found to be higher than the ambient temperature.

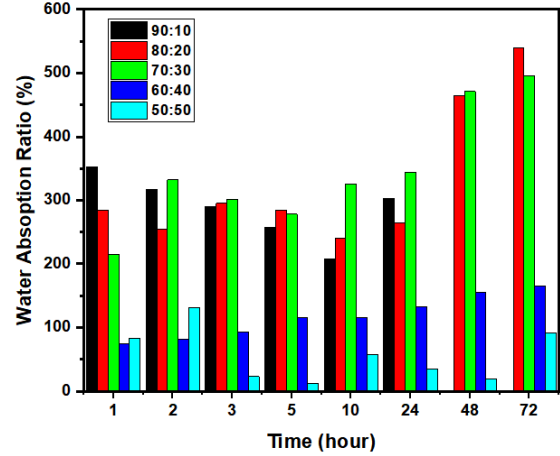


Fig.7. Water Absorption of Films Produced with 40:88 PVA at 40 °C (72 hours)

Conclusions

In this study, PVA/silica gel composite films were successfully synthesized. FT-IR and SEM results showed that homogeneous films were obtained. It was observed that silica in the polymer matrix without creating any clumping. According to experimental results, the viscosity of PVA, the weight ratio of PVA: Silica- gel and the ambient temperature were found the important parameters on water uptake of films. With the increase of PVA viscosity in composite films, water absorption capacity decreased. The lowest water absorption values were obtained with 40:88 PVA. Increasing of silica gel amount in composite films caused less water absorption. While the PVA: silica- gel ratio changed between 90:10-50:50, absorption values of 40:88 PVA/silica gel film changed between 285-19 % after 72 hours. It was observed that the ambient temperature significantly affects water absorption values. For all films dried and kept at ambient temperature, the swelling values (at 40 °C) were found to be higher than the ambient temperature. The lowest water absorption values were obtained with 60:40 and 50:50 (40:88 PVA): silica- gel ratio. In

conclusion, These PVA/silica gel composites can be evaluated as biodegradable films in the food industry.

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