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Optical and pH-Responsive Nanocomposite Film for Food Packaging Application †

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† Presented at the 6th International Electronic Conference on Sensors and Applications, 15–30 November 2019; Available online: https://ecsa-6.sciforum.net/

Published: 14 November 2019

Abstract: In this study, a biocompatible and non-toxic pH-responsive composite film was prepared for food packaging application. The films are composed from polyvinyl alcohol as the main polymeric matrix, nanoclay as a reinforcing component and red cabbage extract as a non-toxic indicator. The prepared films showed lower water uptake values when the amount of nanoclay was increase up to 25 %. It was observed that the films become brittle at high loading of nanoclay (40%). The prepared films exhibited color change in alkaline and acidic medium due to the presence of red cabbage extract which turned pinkish in acidic medium and greenish in alkaline environment. The prepared films were characterized by FTIR and visible spectroscopy. The maximum absorption in acidic medium was (λ_{max} = 527 nm), while a red-shift occurred in the alkaline medium (λ_{max} = 614 nm). Future work will focus on crosslinking of the prepared films to improve their mechanical properties.

Keywords: Nanomposite; pH sensor; optical sensor; colorimetric sensor; food packaging; film; smart film; responsive film; polyvinyl alcohol; red cabbage; nanoclay

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1. Introduction

There is a growing demand for developing smart-responsive packaging films for tracking the freshness of food products, safety enhancement and improving the quality of packaged food during storage, transportation and distribution [1,2]. Smart optical pH-responsive films for food packaging represents one of the most attractive research areas in this field. The pH of the packaged items is prone to change upon long storage or microbial spoilage of the packed food products (e.g., fish, meat and fresh pork sausages) due to pH change in the local microenvironment that surrounds the packed food items. Hence, variety of colorimetric pH indicators immobilized on different polymeric matrices has been employed for optical sensors for detecting the change in the pH of the microenvironment that surrounds the packed food items [3].

The main requirements for preparing pH-responsive films is the safety, which means that films shall be made from safe and biocompatible materials derived from natural resources, which avoids toxicity issues that may result from leaching/ degradation of film components during the application period. Another key feature of the used packaging films is its biodegradability which has a direct impact on the safety of the environment by avoiding use of non-biodegradable materials such as pH-responsive films based on synthetic polymers [4,5]. Natural polymers have been employed for drug delivery applications and hence they are suitable for use as matrix for film packaging materials [6]. Similarly, natural indicators extracted from various plants have been used as non-toxic pH-indicators for preparing the colorimetric and optical pH-responsive films [7,8]. Incorporation of nanomaterials such as nanoclays as a reinforcing matrix enhance the mechanical properties, durability and biodegradability of the bionanocomposite [9,10].

This article represents the preliminary investigation results of using red-cabbage extract as an immobilized indicator in the bionanocomposite film matrix made from polyvinyl alcohol as the main polymer matrix and nanoclay as the reinforcing component. Halloysite nanotubes are biocompatible, cytocompatible and biomaterial which have been employed for sustained release of drugs. Moreover, the presence of nanoclay fillers enhances the biodegradability of the prepared pH-responsive nanocomposite films.

2. Experimental Section

2.1. Materials

Polyvinyl alcohol (PVA) (98-99% hydrolyzed, low molecular weight) was acquired from (Alfa Aesar, Kandel, Germany); Nanoclay –hydrophilic bentonite, particle size ≈25 mm) was acquired from Aldrich (Milwaukee, WI, USA). All other chemicals and reagents were used as received. Red Cabbage was purchased from local stores.

2.2. Preparation of the Films

2.2.1. Preparation of 10% PVA Solution

Ten grams of PVA were dissolved in 90 g distilled water by heating at 60°C with continuous stirring until dissolved completely.

2.3. Preparation of Red Cabbage Extract (RCE)

Approximately, 130 g of chopped red cabbage was soaked in a solution made from 150 mL ethanol, 150 mL water and 4 mL concentrated HCl. The mixture was sonicated for 24 h. The extract solution was filtered off and stored in a glass bottle for subsequent use.

2.4. Film Casting

10 mL of 10% PVA solution was mixed with 1 mL of red cabbage extract and the solution was cast on a glass Petri dish and kept at 50 °C for 24 h. After that, films were wetted with distilled water for 5 min, peeled off carefully and dried at 60 °C for 12 h. The composite films were prepared in a similar way, but with addition of the nanoclay and sonication for 15 min to get a good dispersion of the inorganic matrix. The compositions of the composite films are shown in Table 1.

2.5. Characterization of the Films

2.5.1. Water Uptake

Water uptake measurements were carried out by calculating the weight difference between the dried films and the swollen films for a period of 24 h in distilled water.

2.5.2. Instrumentation

The FT-IR spectra of the neat PVA, neat nanoclay and PVA/nanoclay composite films were recorded in the spectral region of 4000–400 cm^{-1} at a resolution of 4.0 cm^{-1} and 32 scans using the Shimadzu FTIR Prestige-21 spectrophotometer. The visible spectra for films soaked in acidic or basic medium were recorded in the range of 400–1000 nm using Cintra 2020 spectrometer.

3. Results & Discussion

Table 1 presents the chemical composition and physical properties of the prepared films. Water uptake values decrease with increasing the percentage of nanoclay. It is important to mention that the prepared films did not show auto-disintegration inside the water during the measurement period which was a total of 24 h. Regardless, at high percentage of nanoclay loading (50%), the obtained membranes were brittle even in the dry state. Hence, the best obtained result was at 25% loading of nanoclay which corresponds to ≈ 180% water uptake within 24 h period.

Table 1. Chemical composition and water uptake of the fabricated films.

Entry	Film	PVA %	Nanoclay %	RCE* (mL)	WU** %	Physical Appearance
1	PVA	100	-	-	350	Transparent & tough
2	PVA-RCE	100	-	1	345	Transparent & tough
3	PVA-NC-RCE	95	5	1	220	Transparent & tough
4	PVA-NC-RCE	75	25	1	177	Semi-transparent & tough
5	PVA-NC-RCE	60	40	1	130	Semi-transparent & brittle

*(volume of RCE extracts solution/each 10 mL of cast solution)
** Water Uptake.

To study the effect of nanoclay material on the PVA, FTIR spectra of pure PVA, pure nanoclay and that of PVA/nanoclay composite were recorded and the results are presented in Figure 1. The characteristic vibrational peaks with corresponding vibrational assignments are presented in Table 2. The pure PVA and nanoclay showed eight major vibrational peaks (3387, 2940, 2910, 1427, 1335, 1096, 918, and 489 cm^{-1}) and four vibrational peaks (3618, 3441, 1011 and 440 cm^{-1}) respectively. These values are in agreement with the experimental data. The absence of C=O stretching mode at around 1700 cm^{-1} in the spectrum of PVA, shows that the PVA used in this studies is fully hydrolyzed PVA. Though the peak at 1651 cm^{-1} which is attributed to bound water can overlap with carbonyl stretching frequency.

The FTIR spectrum of PVA/nanoclay composite film is presented in Figure 1. The spectrum is dominated by the peaks that are characteristics of both PVA and nanoclay. The peak at 3395 cm^{-1} could be attributed to the overlapping of OH stretching of both PVA and nanoclay.

Table 2. Characteristic FTIR peaks of PVA, Nanoclay and PVA/nanoclay composite.

Neat PVA Film		Neat Nanoclay Powder		PVA-Nanoclay Composite Film (25% Nanoclay)	
Wave Number (cm^{-1})	Functional Group(s)	Wave Number (cm^{-1})	Functional Group(s)	Wave Number (cm^{-1})	Functional Group(s)
3387 2940 2910 1651 1427 1335 1096 918 489	OH stretching Asymmetric CH_2 stretching Symmetric CH_2 stretching H_2O bending CH_2 bending OH rocking OH bending CH_2 rocking CC stretching	3618, 3441 1643 440 1011	OH stretching H_2O bending Si-O bending Si-O stretching	3395 2940 2910 1651 1442 1335 1096 1034 918 489	OH stretching Asymmetric CH_2 stretching Symmetric CH_2 stretching H_2O bending CH_2 bending OH rocking OH bending Si-O stretching CH_2 rocking CC stretching

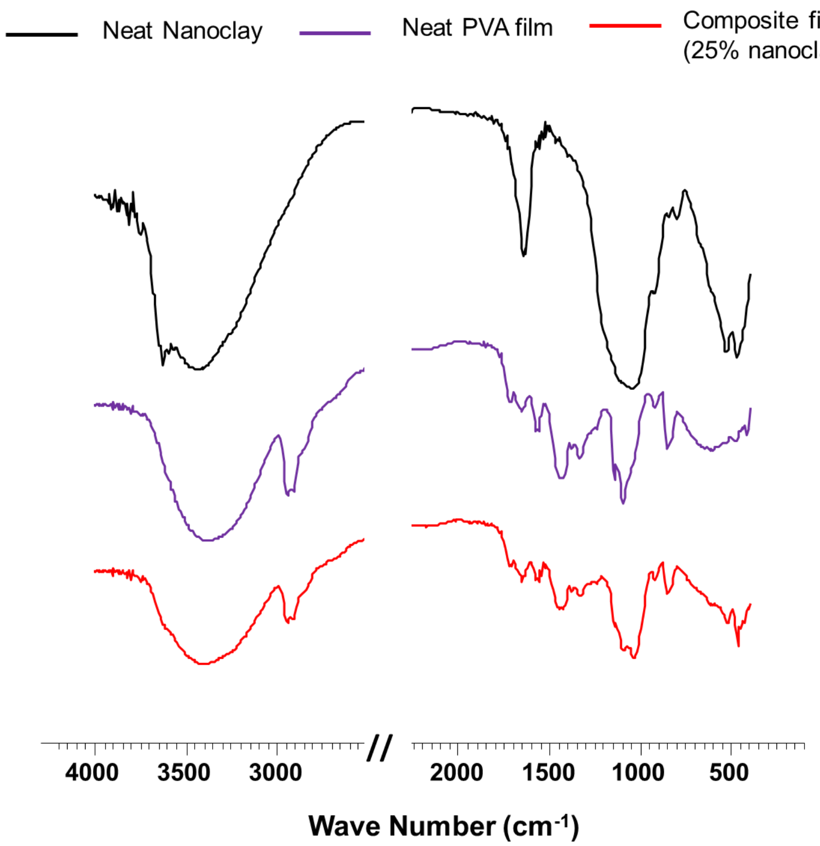

Figure 1. FTIR spectra of the prepared samples.

The obtained films showed pH-responsiveness during the shift from alkaline to acidic medium or *vice versa*. As illustrated in Figure 2, the film has distinctive pinkish color in the acidic medium, while it turns into a greenish color in alkaline medium. This observation is reflected in the acquired spectra of the corresponding films in acidic/alkaline medium, Figure 2. The absorption maxima of the film in the acidic medium is (λ_{max} = 527 nm), while it has red-shifted in the alkaline medium to (λ_{max} = 614 nm). The observed shift red-shift in λ_{max} could be attributed to the structural changes in the conjugated ring of the cabbage anthocyanins. Hence, the prepared films can be used for applications where there will be a color change during the pH change, for example, when the food freshness is altered upon long storage / improper storage conditions.

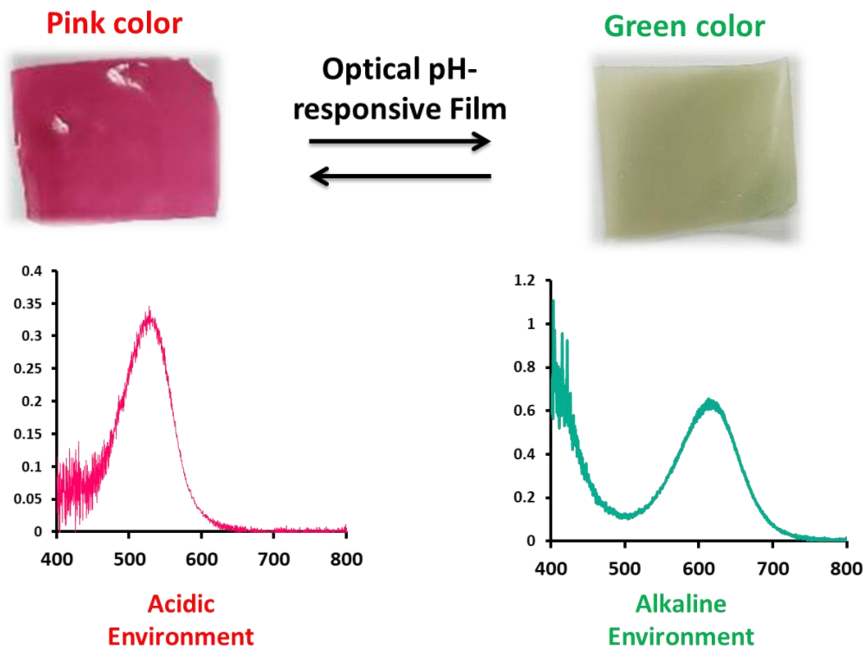

Figure 2. Digital images of the pH-responsive composite films containing 25% nanoclay, in acidic medium at pH ≈ 2 (left) and alkaline medium pH ≈ 12 (right). The corresponding spectrograms in visible region are displayed underneath each film.

4. Conclusions

Incorporation of nanoclay into the PVA films is an effective way for reducing the water uptake values of polyvinyl alcohol films. The addition of red cabbage extract as a natural indicator was effective to provide a visual tool for observing the change in pH medium of the surrounding environment. However, further work has to be carried out to improve the mechanical properties of the membranes by adding a suitable and non-toxic crosslinking agent which will allow for binding nanoclay to PVA matrix in the prepared nanocomposite films.

Author Contributions: conceptualization, N.A.; methodology, Z.S., Y.U., A.Y., A.H, and A.B., AZ; software, AY., AH.; formal analysis, N.A., Y.U. and E.R.; writing—original draft preparation, N.A.; visualization, S.A.; supervision, I.A.

Acknowledgments: Authors would like to express their appreciations to Jubail Industrial College for using the research facilities inside the chemical and process engineering technology department.

Conflicts of Interest: The authors declare no conflict of interest.

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