

# Optical and pH-Responsive Nanocomposite Film for Food Packaging Application <sup>†</sup>

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**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 increased 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 an alkaline environment. The prepared films were characterized by FTIR and visible spectroscopy. The maximum absorption in acidic medium was ( $\lambda_{\max} = 527$  nm), while a red-shift occurred in the alkaline medium ( $\lambda_{\max} = 614$  nm). Future work will focus on the 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 the development of smart-responsive packaging films for tracking the freshness of food products, enhancing safety, and improving the quality of packaged food during storage, transportation, and distribution [1,2]. Smart optical pH-responsive films for food packaging represent one of the most attractive research areas in this field. The pH of the packaged items is prone to change during 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, a variety of colorimetric pH indicators immobilized on different polymeric matrices has been employed for optical sensors for detecting changes in the pH of the microenvironment that surrounds the packed food items [3].

The main requirements for preparing pH-responsive films is safety, which means that films should 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 packaging films used is their biodegradability, which has a direct impact on the safety of the environment by avoiding the 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 a matrix for film packaging materials [6]. Similarly, natural indicators extracted from various plants have been used as non-toxic pH-indicators for preparing 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 a bionanocomposite film matrix made from polyvinyl alcohol as the main polymer matrix and nanoclay as the reinforcing component. Halloysite nanotubes are biocompatible and cytocompatible biomaterial that have been employed for the 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  $\approx 25$  nm) 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 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

Ten milliliters 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 the 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.

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

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

\* (volume of Red Cabbage Extract (RCE) solution/each 10 mL of cast solution); \*\* Water Uptake.

### 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 FTIR spectra of the neat PVA, neat nanoclay, and PVA/nanoclay composite films were recorded in the spectral region of 4000–400  $\text{cm}^{-1}$  at a resolution of 4.0  $\text{cm}^{-1}$  after 32 scans using a 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 a Cintra 2020 spectrometer.

## 3. Results and Discussion

Table 1 presents the chemical compositions and physical properties of the prepared films. Water uptake values decrease with the increased 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 a 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  $\approx 180\%$  water uptake within a 24 h period.

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  $\text{cm}^{-1}$ ) and four vibrational peaks (3618, 3441, 1011, and 440  $\text{cm}^{-1}$ ), respectively. These values are in agreement with the experimental data. The absence of C=O stretching mode at around 1700  $\text{cm}^{-1}$  in the spectrum of PVA shows that the PVA used in this study is fully hydrolyzed PVA, though the peak at 1651  $\text{cm}^{-1}$ , which is attributed to bound water, can overlap with carbonyl stretching frequency.

**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 ( $\text{cm}^{-1}$ )	Functional Group(s)	Wave Number ( $\text{cm}^{-1}$ )	Functional Group(s)	Wave Number ( $\text{cm}^{-1}$ )	Functional Group(s)
3387	OH stretching			3395	OH stretching
2940	Asymmetric $\text{CH}_2$ stretching			2940	Asymmetric $\text{CH}_2$ stretching
2910	Symmetric $\text{CH}_2$ stretching	3618	OH stretching	2910	Symmetric $\text{CH}_2$ stretching
1651	$\text{H}_2\text{O}$ bending	3441	$\text{H}_2\text{O}$ bending	1651	$\text{H}_2\text{O}$ bending
1427	$\text{CH}_2$ bending	1643	Si-O bending	1442	$\text{CH}_2$ bending
1335	OH rocking	440	Si-O stretching	1335	OH rocking
1096	OH bending	1011		1096	OH bending
918	$\text{CH}_2$ rocking			1034	Si-O stretching
489	CC stretching			918	$\text{CH}_2$ rocking
				489	CC stretching

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

The obtained films showed pH-responsiveness during the shift from alkaline to acidic medium, and vice versa. As illustrated in Figure 2, the film has a distinctive pinkish color in the acidic medium, while it turns to a greenish color in the alkaline medium. This observation is reflected in the acquired spectra of the corresponding films in acidic/alkaline medium, as seen in Figure 2. The absorption maxima of the film in the acidic medium is ( $\lambda_{\text{max}} = 527 \text{ nm}$ ), while it has red-shifted in the alkaline medium to ( $\lambda_{\text{max}} = 614 \text{ nm}$ ). The observed red-shift in  $\lambda_{\text{max}}$  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.

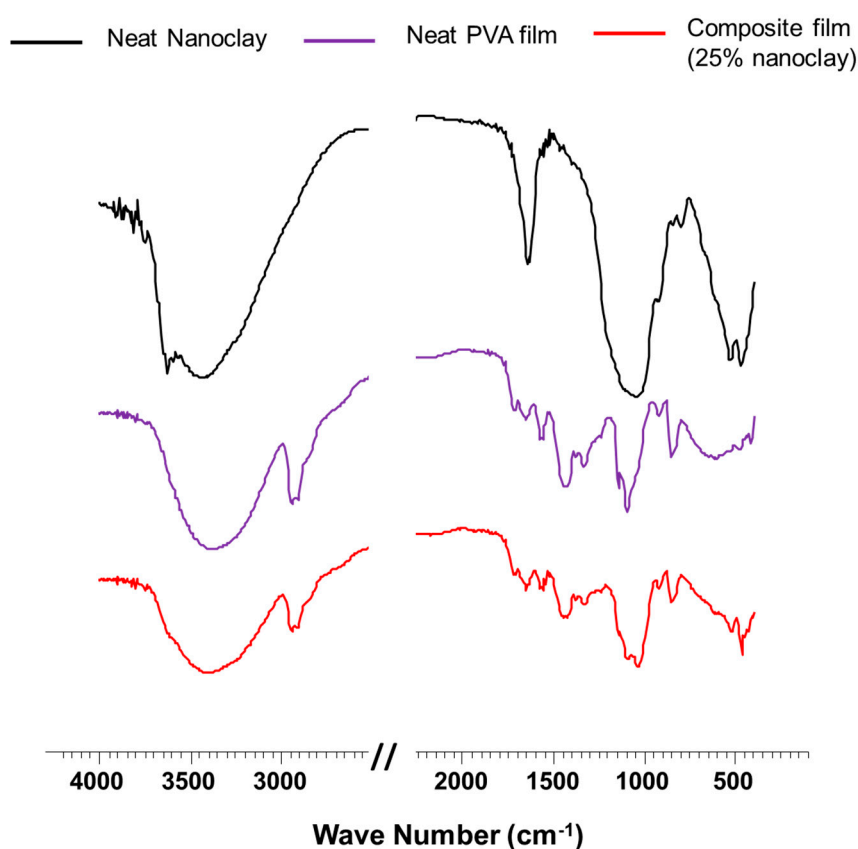


Figure 1. FTIR spectra of the prepared samples.

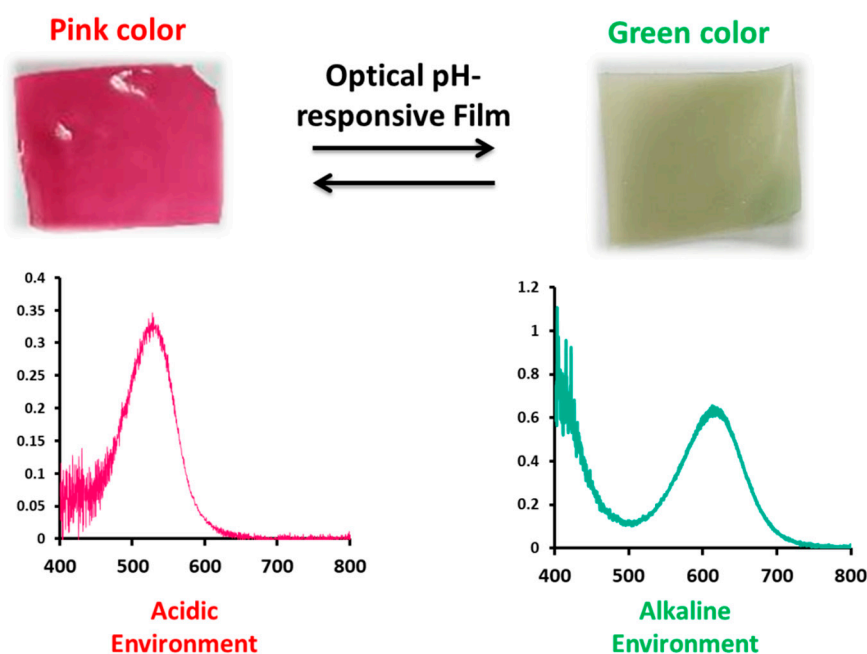


Figure 2. Digital images of the pH-responsive composite films containing 25% nanoclay, in acidic medium at  $\text{pH} \approx 2$  (left) and alkaline medium  $\text{pH} \approx 12$  (right). The corresponding spectrograms in the visible region are displayed underneath each film.

#### 4. Conclusions

Incorporation of nanoclay into PVA films is an effective way to reduce 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 the 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 the binding of nanoclay to the PVA matrix in the prepared nanocomposite films.

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

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