Thermomechanical, Morphological and Spectroscopic Investigations of Orange Peel Extract Doped PVA Films

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Abstract

The present study aims to evaluate the influence of orange peel extract on properties of the PVA films. Using the solvent casting technique, orange peels extract doped PVA films were prepared with varying concentrations. The prepared films were examined for their mechanical, thermal, and phase morphological properties using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and a universal testing machine (UTM). Furthermore, Fourier transform infrared spectroscopy (FTIR) was used to examine the interaction between the blend components. The study's findings corroborated previous observations that elongation at break has grown substantially while tensile characteristics have not improved considerably. The SEM micrographs revealed the phase separation at increased concentration, which could explain the lower tensile characteristics. The PVA films' thermal stability has been somewhat improved, according to thermogravimetric result. The interaction among the blend films was validated by the FTIR study's results. Furthermore, work can be extended to antimicrobial, contact angle, solubility, biodegradation, swelling and food compatibility of the films.

Keywords: Orange peel extract, PVA, Mechanical Properties, Thermal properties, Morphology.

1. Introduction

Increasing environmental concern led to an extensive research on using renewable resources to create sustainable, biodegradable or edible food packaging systems [1-3]. Now a day’s maximum research has been concentrated towards the edible and biodegradable films [4]. Over the past two decades, edible films or coatings have been studied because of their abilities to retard gas barrier properties including moisture, oxygen, aromas and solute transports [2]. With this concern, paper and cardboard can be used as eco-friendly packaging polymers but moisture can act as the barrier. This property can be improved by making use of polymers. The films prepared from natural plant extract have the potential applications in packaging systems and they can be commercially explored to extend the shelf life of food products.

Poly (vinyl alcohol) (PVA) is a water- soluble, non-toxic, semi-crystalline, synthetic polymer. PVA has excellent film–forming and emulsifying properties [5-7]. Due to ease of preparation, biodegradability, good mechanical properties and chemical resistivity, PVA is used in various biomaterial applications. The use of PVA finds varied applications in control drug delivery system, membrane preparation, recycling of polymers, pharmaceutical industry, packaging and biomedical applications [8-15].

Orange (Citrus sinensis) belongs to family Rutaceae. It is one of the commercial fruit crops grown worldwide. Orange is well known from Southern China to Indonesia from which they were spread to India. Nearly 3.23 million tons of citrus fruits were produced in Egypt of which 2.14 million tons were found to be orange in 2008 [16]. Citrus fruits were mainly used by juice processing industries while the peels were generally wasted. Very large amounts of by-product wastes, such as peels were formed every year [17-18]. The orange peels are rich in nutrients, which can also be used for the food supplements [19]. The orange peel waste product can be used for the production of polymers films which can improve the antimicrobial activity in films. The present study aims to prepare natural orange peel extract doped biodegradable PVA blend films and study the effect of orange peel extract on PVA films. The study also aims to investigate the multifunctional properties of blend films in view of food packaging applications.

2. Materials and Methods

Poly (vinyl alcohol) (PVA) was purchased from Central Drug House (CDH), New Delhi. Alcohol and double distilled water used as a solvent throughout the experiment.

2.1. Extraction of Orange Peel

Fresh orange peels (OP's) were collected and dried in a shade to remove moisture content. The OP's were then mechanically powdered and extraction was conducted in Soxhlet apparatus. 30g of dry OP's powder was mixed with 150 mL alcohol (solvent) and extraction was carried out for 6 hours under 45 ^{o}C. The colour of crude extract obtained was yellowish orange.

2.2. Preparation of the Blend Films

Pure PVA and different weight percent of OP's extract doped PVA blend films were prepared by using solvent casting technique (Table 1). 2g of PVA was weighed accurately and dissolved in 100 mL of double distilled with constant stirring up to 2 hours. The OP's extract dissolved in alcohol (1g in 100 mL alcohol 1% solution). Keeping PVA constant (2g) different mL OP's extracts solutions were

mixed and stirred overnight to get clear homogenous solution. After ensuring complete dissolution blend solutions were then poured onto Petri dishes and solvent was allowed evaporate at room temperature. To ensure complete drying films were then placed in hot air oven at 45 oC. The films were peeled off from the Petri dish and stored in desiccators until use.

Table 1: Composition of films

Film Code	PVA (mL)	Orange Peel Extract (mL)
PVA	100	0
PVA/OPs-1	100	5
PVA/OPs-2	100	10
PVA/OPs-3	100	15
PVA/OPs-4	100	20

2.3. Characterizations

2.3.1. Film Thickness

The thickness of prepared blend films were measured using hand held Mitutoya Dial Gauge (Japan) with accuracy of 0.001mm. Various thickness measurements were taken on each film at different locations and averaged. The average value of each blend film was then used to assess the mechanical properties of prepared blend films. Average thickness of the blend films was found to be 0.072 mm.

2.3.2. Mechanical Properties

A Universal testing machine (LLOYD Instrument) was used to check the tensile strength (T_S), young's Modulus (Y_m) and elongation at break (E_b) according to ASTM D882-91 (ASTM, 2009) at room temperature in air. The film sample size of 10 cm x 2.5 cm cut from the film for analysis.

2.3.3. Scanning Electron Microscopy

The miscibility among the blend components is an important factor to develop a new material with desired properties. To know the miscibility among the constituents of the prepared blend films, Scanning Electron Microscopy (SEM) was Used (JOEL JSM-6360) and operated at an acceleration voltage of 10 kV. Before the analysis, film pieces were mounted on metal stub using a double-sided sticky tape and then coated with a thin layer of gold to avoid charging under electron beam and allowing surface visualization.

2.3.4. Thermogravimetric Analysis

The thermal properties of pure and prepared blend films were measured using thermogravimetric analyzer (SDT Q600 V20.9 Shimadzu, Tokyo) from 30 ^{o}C to 700 ^{o}C in an inert N_2 environment (flow rate 100 mL/min) at heating rate of 10 ^{o}C/min. The sample mass of 5-10 mg was used to study the thermal properties.

2.3.5. FT-IR Spectroscopy

The prepared blend films were subjected to FTIR spectroscopy to understand the possible inter molecular interactions. The FTIR spectra of the films were recorded using an Attenuated Total Reflection (ATR) method in IR spectrometer (FT-IR-ATR, Prestage 21, Shimadzu, Japan). The samples were subjected to analysis between 400 and 4000 cm^{-1} with resolution of 4 cm^{-1}.

3. Result and Discussions

3.1. Mechanical Properties

The influence and contribution of OP's extracts on final properties of the PVA blend films were analyzed with Universal testing machine and results were summarised in Table 2. Binary blend films of PVA/OP's extracts initially showed increased T_S and Y_m (PVA/OP-1 to PVA/OP-2). As concentration of OP's extract increased in PVA film, T_S and Y_m showed descending order (in PVA/OP-3 to PVA/OP-4). Further, elongation at break (E_b) showed significantly increased value with increasing concentration of OP's extracts. The decrease in mechanical properties attributed to the lower interaction and compatibility between PVA and OP's extracts. In addition, the significant influence of OP's extracts on PVA was observed, which confirmed the decreased T_S, Y_m and increased E_b when compared to pure PVA (T_S 18.20 MPa, Y_m 19 MPa and E_b 480.38 in PVA/OP's-4). The results of mechanical study revealed that binary blend films PVA/OP's extracts showed initially increased mechanical properties and decreased with increase in the OP's extracts.

Table 2: Mechanical properties of Pure PVA and PVA/OPs Blend films

Film Code	Thickness (mm)	Tensile Strength (Ts)	Young's Modulus (Ym)	Elongation at Break
PVA	0.091	21.70	24.48	394.32
PVA/OP's-1	0.07	22.85	25.66	410.55
PVA/OP's-2	0.08	21.10	22.79	450.07
PVA/OP's-3	0.07	19.38	20.91	471.04
PVA/OPs-4	0.06	18.20	19.87	480.38

3.2. Scanning Electron Microscopy

The compatibility and miscibility among the blend components were examined by using Scanning electron microscopy (Figure 1). The SEM images of PVA/OP's extracts blend films showed different phase morphology compared to pure PVA. With increase in concentration of OP's extracts heterogeneous morphology and phase separation was observed. Incorporation of OP's extracts onto PVA film has direct influence on final mechanical properties exhibiting heterogeneous phase morphology. In addition, with increase in concentration of OP's extracts, aggregation of particle like structures was observed in films leading to the phase separation.

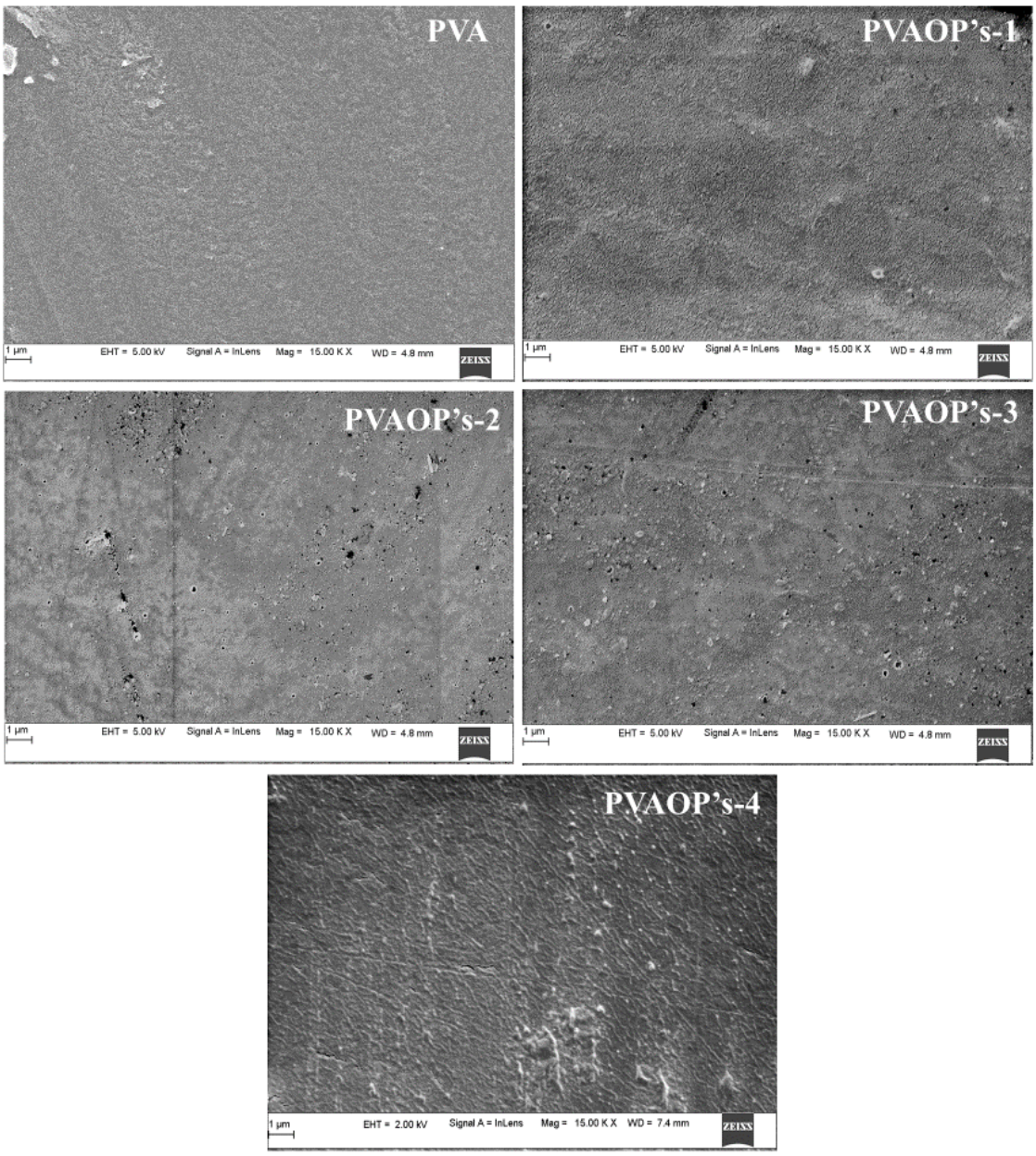
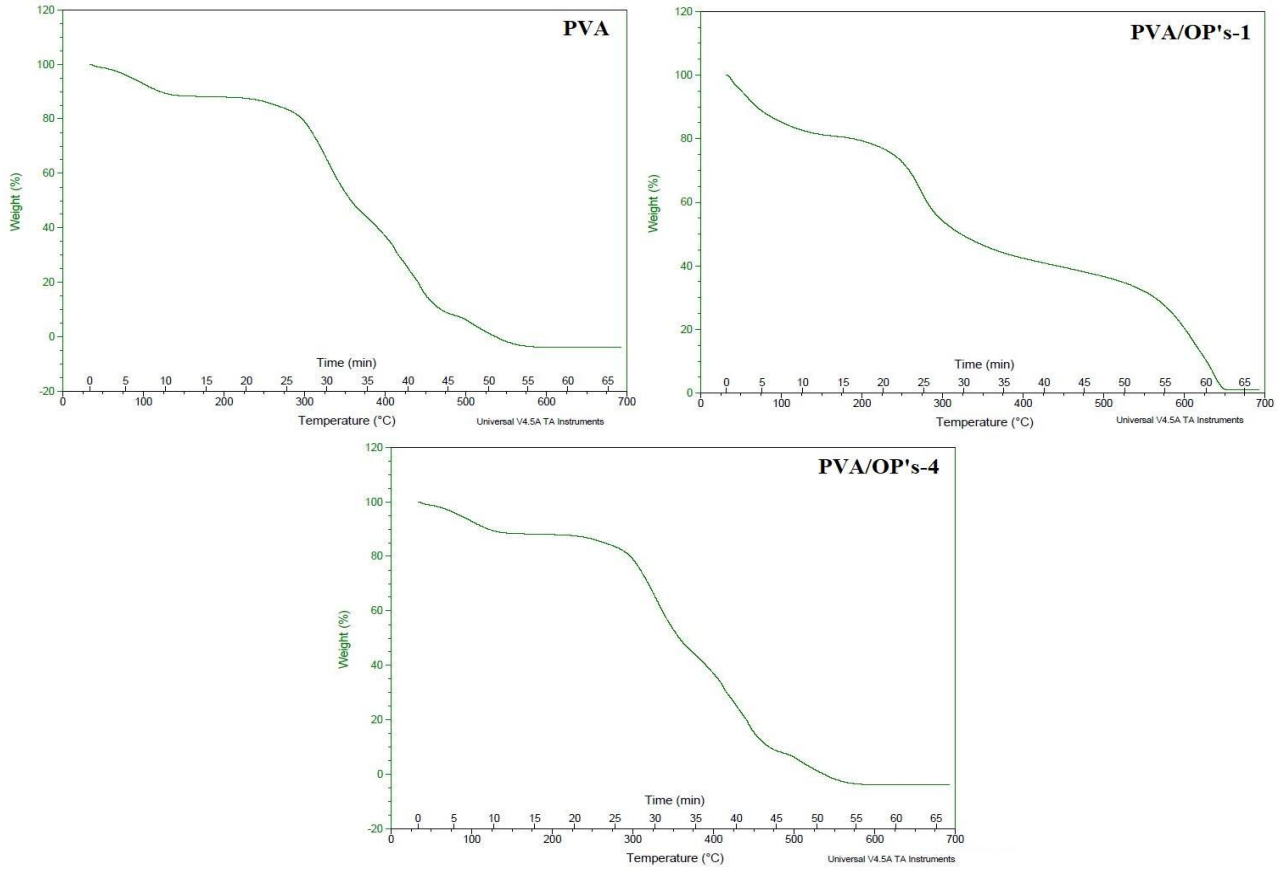


Figure 1: SEM Micrographs of PVA and PVA/OP's Blend Films

3.3. Thermogravimetric Analysis

Thermal stability of the films was evaluated with thermogravimetric analysis. Figure 2 presents the thermogram of pure PVA and PVA/OP's blend films. Thermogram of pure PVA showed three step degradation patterns. The initial degradation step occurred at 25 ^{o}C to 143 ^{o}C due to the evaporation of physically absorbed water [20-21]. The second weight loss notice at 143 ^{o}C to 228 ^{o}C, attributed to the thermal degradation of PVA molecule. The third weight loss observed in the range of 228 ^{o}C to 577 ^{o}C, attributed to the release of by-product generated second degradation step of PVA respectively. The results were close agreement with other researchers [22].

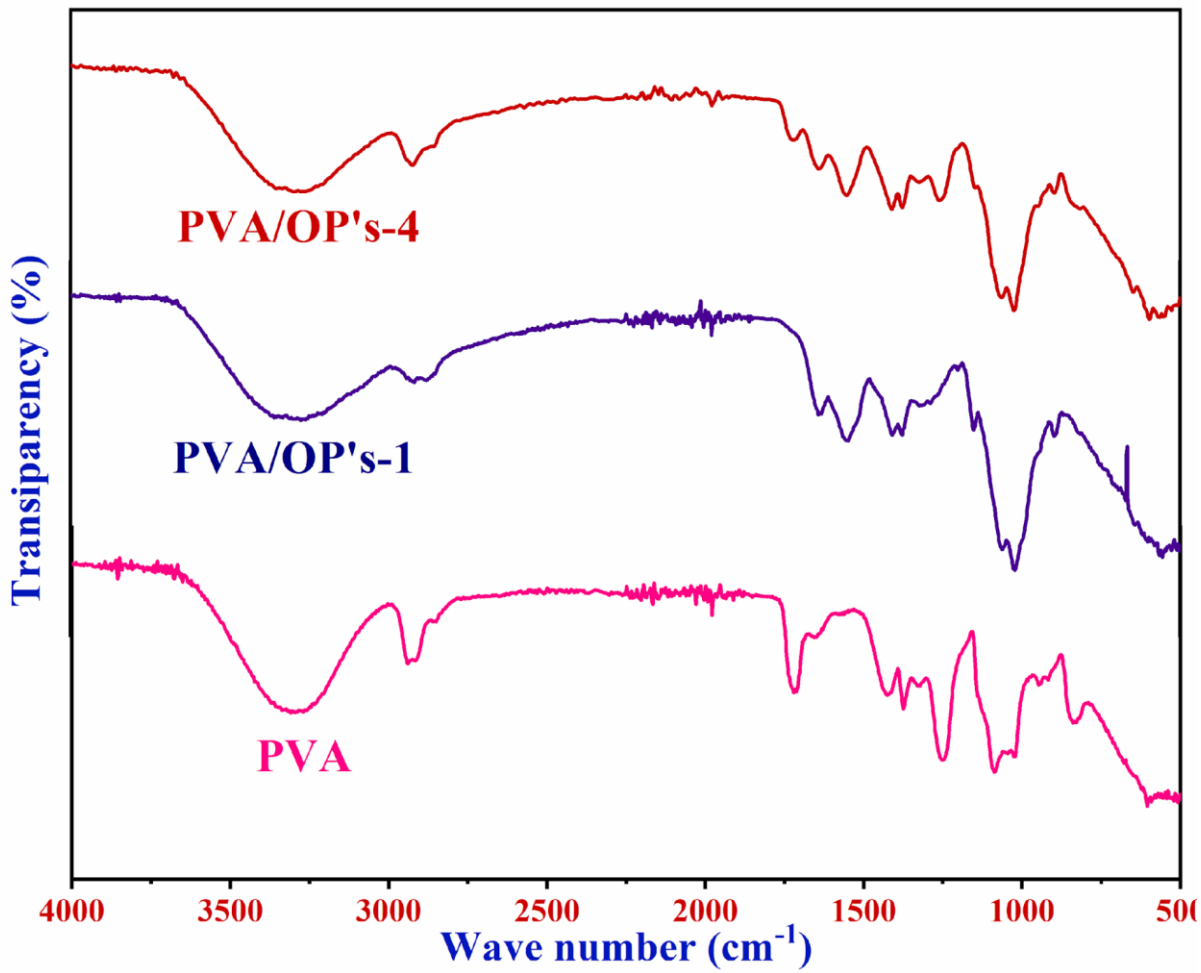
The PVA film showed increased thermal stability with incorporation of OP's extracts. In all blend films three step degradation patterns was observed. The first degradation step occurred at 30 ^{o}C to 130 ^{o}C, it is due to evaporation of water molecules. The second degradation step occurred between 230 ^{o}C to 490 ^{o}C. During this maximum weight loss observed which is attributed to the fully destruction of blend films due to the increased number of intermolecular chains with lower interaction among the PVA and OP's extracts. At last, third degradation step was noticed at 490 ^{o}C to 599 ^{o}C, it could be due to the complete degradation of blend components.



3.4. Fourier Transform Infrared Spectroscopy

The FTIR spectra of PVA and PVA/OP blend films were presented in figure 3. The FTIR spectra of pure PVA showed characteristic peak at 3336 cm^{-1} [23] due to the non- bonding stretching of OH group. The peak occurred at 2850-3000 cm^{-1} [24] assigned to the C-H stretching vibration. The peak observed at 1141 cm^{-1} is one of the important peaks which explains the semi-crystalline nature of PVA and shows many domains for cross-linking [25- 27]. In addition, peak observed at 1251 cm^{-1} and 842 cm^{-1} due to the C-C stretching and C-H rocking. The peak observed at 1712 cm^{-1}assigned to the C=O stretching vibration of PVA.

In binary blend films of PVA/OP's extract, the stretching of vibration occurred at 3279 cm^{-1} is due to the shifting of -OH stretching vibration of PVA indicating that intermolecular interaction. Similarly, the characteristic peak of PVA shifted to the 2926 cm^{-1} in PVA/OP's extract blend films. The shifting of peak observed at 1102cm^{-1}, 826 cm^{-1}, 1731cm^{-1} confirmed the interaction between PVA and OP's extracts. The results of FTIR spectra evidenced that some of the peak values were shifted to the lower value and some are merged compared to pure PVA. This confirms the specific interaction existed between PVA and OP's extracts.



4. Conclusion

In the present study PVA and PVA/OP's extracts blend films were successfully prepared by solvent casting technique and characterized with different instrumental techniques. The results of mechanical, morphological and thermal study confirmed that mechanical properties initially increased with addition of OP's extracts at lower concentration presenting homogenous phase morphology. At higher concentration decreased mechanical properties were observed with heterogeneous phase morphology. The results of FTIR study showed intermolecular interaction between PVA and OP's extracts. Therefore, prepared blend films can be used as potential packaging material in future.

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