

Smart Film Based on Polylactic Acid, Modified with Polyaniline/ZnO/CuO: Investigation of Physicochemical Properties and its use of Intelligent Packaging of Orange Juice

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Abstract

In this study, a biodegradable/conducting film based on polylactic acid (PLA) modified with polyaniline, zinc oxide and copper oxide (PLA/PAn/CuO/ZnO) was prepared. The effect of polyaniline, zinc oxide and copper oxide on the electrical, physicochemical, antioxidant and antimicrobial properties of polylactic acid films by different techniques such as SEM, FTIR, TGA, etc. were investigated. Electricity conductive films were used for intelligent packaging of orange juice. The chemical and microbial properties of orange juice and the electrical conductivity of packaging films during storage time (56 days) were investigated. The results showed that the effect of polyaniline, zinc oxide and copper oxide greatly increased the antioxidant and antimicrobial properties of polylactic acid film. Polyaniline gave the film good electrical conductivity, but zinc oxide and copper oxide had no significant effect on it. The active film used to package the orange juice increased the chemical and microbial viability of the orange juice. The electrical resistance of the conductive films used for packaging increased over time and a significant mathematical relationship was established between storage time and changes in electrical resistance, which was used to estimate the shelf life and expiration date of orange juice. Examination of the performance of the films showed that these films with an accuracy of over 90% have the ability to estimate the storage time of orange juice. Electricity conductive/antimicrobial/antioxidant film based on polylactic acid as an active and intelligent film has the ability to increase the shelf life and detect spoilage of orange juice.

1. Introduction

Biodegradable polymers are a special type of polymer that decompose by bacterial decomposition to form by-products such as carbon dioxide, water, biomass, and mineral salts. These polymers are made naturally and synthetically and are mainly composed of functional groups of ester, amide and ether. Their properties and decomposition mechanism are determined by their exact structure. These polymers are often synthesized by compaction reactions, open ring polymerization, and metal catalysts. Packaging materials made from environmentally friendly materials have been introduced as a green alternative in recent decades, in which edible films have attracted more attention due to their environmentally friendly properties, wide variety and availability, non-toxicity and low cost (Gouveia et al., 2019; Malathi et al., 2014; Pirsá, 2020; Pirsá et al., 2020a). Polylactic acid (PLA) is obtained from renewable sources such as cornstarch and starch or sugarcane roots. Polylactic acid is mainly produced through two processes of condensation and polymerization. The most common method is the polymerization process. In this process, by combining metal catalysts with lactide, larger PLA molecules are formed. In the condensation process, the main difference with the polymerization process is the temperature during the process, and as a result, by-products are released. The special advantage of polylactic acid over other polymers is its biodegradation, which is generally degraded by a single-step process with a bacterial attack on the polymer. They are easily degraded in atmospheres with high humidity and temperatures of 70 – 55 °C (Erdohan et al., 2013; Tawakkal et al., 2014; Pirsá & Asadi, 2021). Conductive polymers are polymers with conjugated π electrons ($C = C$) that have electronic properties. This group of polymers is easily oxidized

and reduced compared to conventional polymers. Conductive polymers such as polypyrrole, polythiophene and polyaniline have complex dynamic structures that are used in intelligent materials research. The application of electrical stimuli can cause drastic changes in the chemical, electrical and mechanical properties of conductive polymers (Kim et al., 2020; Wang et al., 2020a; Sheikh-Mohseni & Pirsa, 2016; Alizadeh et al., 2015a; Alizadeh et al., 2015b; Pirsa & Nejad., 2017; Pirsa et al., 2016). Polyaniline is one of the oldest synthetic conductive polymers, whose high electrical conductivity has attracted much attention. Polyaniline is basically known as a polymer redox and is prepared chemically and electrochemically in an acidic environment, the choice of method depends on the type of application. If thin films, better properties and purity are needed, electrochemical method is recommended. Due to its diverse structure, thermal and radiant stability, low cost, ease of synthesis and conductivity, polyaniline is used in various fields, including smart polymers, smart packaging, microelectronics, corrosion coatings, sensors and electrodes for batteries. Today, the construction and development of low-cost smart films based on cheap, lightweight, flexible and electrically conductive polymeric materials have received much attention (Liu et al., 2014; Pyarasani et al., 2019; Mohammadi et al., 2019; Alizadeh et al., 2017; Pirsa, 2013). Nanoparticles are usually spherical particles with dimensions of 1-100 nm. In these particles, the surface to volume ratio is high, which makes them more reactive. Research has shown that zinc oxide and copper oxide show greater antibacterial properties at the nanoparticle scale. Zinc oxide and copper oxide can inhibit the production of acid by *Streptococcus mutans*. Even other research has proven its antimicrobial effect on Gram-positive and negative bacteria. Therefore, the presence of these nanoparticles in food packaging films controls bacterial spoilage and increase food shelf life (Widiarti et al., 2017; Mohamed et al., 2020; Rezaei et al., 2020). Consumption of natural juices and beverages is much healthier than consumption of industrial juices, but natural juice preservation methods are more difficult because they do not use preservatives. Orange juice is a very popular fruit juice that can be easily prepared at home. Orange juice is rich in vitamin C (ascorbic acid), potassium, thiamine, phosphorus, vitamin B9 and vitamin B6. The less orange juice is exposed to the air, the longer it retains its original taste. Microbial and bacterial spoilage, mold or fungus can reduce the quality of orange juice. If the juice changes color or smells or the juice container contains visible molds, it should be strictly avoided (Perez-Cacho & Rouseff, 2008; Wibowo et al., 2015). Smart/active packaging is one of the new methods of food packaging. In these methods, packaging polymers contain antioxidant and antibacterial active ingredients (such as copper nanoparticles and zinc oxide metal nanoparticles) that protect packaged food against oxidative and microbial spoilage. On the other hand, these polymers contain an intelligent component that can intelligently detect physical, chemical or microbial changes that occur inside the food package. The intelligent part of these polymers can report spoilage of food or major changes inside the food package to the consumer by color changing, electrical conductivity changing or physical changing (Sobhan et al., 2020; Tyuftin & Kerry, 2020; Chavoshizadeh et al., 2020; Asdagh & Pirsa, 2020; Pirsa, 2016; Pirsa et al., 2020b).

In this study, in order to actively and intelligently package orange juice, a polylactic acid film modified with polyaniline/CuO/ZnO was used. The phytochemical properties of the prepared film were investigated. The effect of the prepared film on increasing the shelf life of orange juice and identifying

the spoilage of orange juice was investigated. The results confirmed the ability of the prepared film to control the deterioration of orange juice (active film) and detect its corruption (smart film).

2. Materials And Methods

2.1. Chemicals

Polylactic acid granules with 99% purity were prepared from the Khatam Polymer Company (Iran, Tehran). Copper oxide nanoparticles (with 99% purity, and particle size of 30–60 nm) and zinc oxide (with 99% purity, and particle size of 30–70 nm) were purchased from the Nanogiluzac Company (Iran, Tehran). 2, 2-diphenyl-1-picrylhydrazyl (DPPH), a variety of salts and other chemical compounds were prepared by Merck (Germany) and Sigma-Aldridge (USA) and used without re-purification. Microbial strains used include *Escherichia Coli* ATCC13706, *Staphylococcus aureus* ATCC6538 was prepared from the collection center of Tehran Industrial Microorganisms. Mueller-Hinton Agar and Serum Agar culture media were prepared from QUELAB (Canada). The culture media of potato dextrose agar and plate agar plate were prepared from Liofilchem Co. (Italy). Olinda Valencia oranges were purchased from the local market in Tabriz (Iran).

2.2. Preparation of polylactic acid film and its composites

Solvent casting method was used to prepare polylactic acid/polyaniline/CuO/ZnO. For this purpose; the polylactic acid granules were dried in a vacuum oven at 60 °C for 24 hours. Certain weighted amounts of copper oxide and zinc oxide nanoparticles (according to Table 1) were added to the Erlenmeyer flask containing 100 ml of chloroform and sonicated at 25°C for 30 minutes. Then 4 g of PLA granules was added to this mixture and stirred for 6 hours by a magnetic stirrer at 400 rpm. Then 0.1 M of aniline was added to the mixture and the solution was again placed in an ultrasonic bath at 25°C for 20 minutes and then stirred on a magnetic stirrer for 2 hours. Finally, the solution was poured into a glass plate with a diameter of 10 cm and kept at room temperature for 24 hours. After evaporation of the solvent, the prepared films were separated from the plate and placed at room temperature for 6 hours. After removing the films from the plates, the films were immersed in 0.2 M FeCl₃ oxidizing solution (50 ml) for 18 hours. At this time, the aniline in the film structure was oxidized by the FeCl₃ oxidant and converted to polyaniline. In this process, the color of the film changed from white to black. After that, the films were removed from the oxidizing solution and dried at room temperature for 24 hours and stored in special zippered bags until the test. Figure 1-A shows some PLA and its composite films.

Table 1

A. List of films prepared based on the central composite design

Film	Factor 1: ZnO (%)	Factor 1: CuO (%)
1	0	0
2	1	0
3	0	1
4	3	0
5	0	3
6	1	3
7	3	1
8	1	1
9	3	3
10	1	1
11	1	1
12	1	1
13	1	1

Table 1

B. List of films prepared based on factorial design

Film	Factor 1: ZnO (%)	Factor 1: CuO (%)
1	0	0
4	3	0
5	0	3
9	3	3

Table 1-C. List of tests performed for packaging orange juice according to factorial design

Run	Film type	Storage time (Day)			
1	PLA/PAn				
2	PLA/ PAn /CuO	0	7	28	56
3	PLA/ PAn /ZnO				
4	PLA/PAn/CuO/ZNO				

2.3. Physicochemical tests of polylactic acid films

2.3.1. Thickness

The thickness of the films produced were randomly measured by digital micrometers (Mitutoyo, Tokyo, Japan) at 10 points from the film samples at 25 ° C and 50% relative humidity and the average of the numbers obtained was calculated.

2.3.2. Water uptake

To calculate the water uptake of the films, the samples were cut to 2.5×2.5 cm and placed in an oven at 50°C for 24 hours. After initial weighing (W_0) of the samples, they were transferred to a desiccator containing saturated calcium sulfate solution (relative humidity 35% and temperature 25°C). Then the weight of the samples was measured over time until a constant weight (W_1) was obtained and the amount of water uptake (WU) was obtained by the following Equation (Kampeerappun et al., 2004).

$$WU(\%) = \frac{w_0 - w_1}{w_0} \times 100$$

1

2.3.3. Moisture content (MC)

To measure the moisture content of the film; First, the tested film was prepared in the shape of 2.5×2.5 cm² and qualified in desiccator containing calcium sulfate and the film weight was measured (W_0). After that the film was dried in an oven at 105°C for 24 hours and weighted again (W_1). The difference in primary (W_0) and secondary (w_1) weights was reported as the moisture content of the film and MC was calculated with following Equation (Jiang et al., 2010).

$$MC(\%) = \frac{w_0 - w_1}{w_0} \times 100$$

2

2.3.4. Solubility in water

To measure the solubility in water, film samples with dimensions of 2×4 cm were prepared. To obtain the initial weight of the film, it was placed in an oven at 105°C for 24 hours and the initial weight (M1) was measured. Then, the film was placed in Falcons containing 50 ml of distilled water for 24 hours at 25°C. After that, the film was filtered using a filter paper and placed in the oven at 105 ° C again to reach a constant weight (M2) and the solubility was calculated based on the following Equation (Gontard et al., 1994).

$$\text{Solubility}(\%) = \frac{M_1 - M_2}{M_1} \times 100$$

3

2.3.5. Water vapor permeability (WVP)

The rate of Water vapor permeability (WVP) of the films was determined based on the ASTM E95-96 method at 25°C. In this method, 3 g of calcium sulfate was poured into a special container and the film was placed in the mouth of the container and the mouth of the container was completely sealed. The glass vial was then placed in an environment containing saturated calcium nitrite with a relative humidity of 75%. The weight difference of the vials was measured every 6 hours for 3 days. The line curve of container weight-time were plotted. The water vapor transfer rate (WVTR) was calculated by dividing the slope of the line by the surface of the test films. Water vapor permeability was also obtained from the following equation (ASTM, 1995).

$$WVTR = \frac{\text{Lineslope}}{\text{Filmsurfacearea}}$$

4

$$WVP = \frac{WVTR}{\Delta p} \times \text{filmthickness}$$

5

Where, m is the rate of weight gain after the test time; t is the test time; L is the film thickness; A is the film surface area and Δp is the difference steam pressure between outside and inside the test vessel (3169 kPa).

2.3.6. Antioxidant activity

For this purpose, 0.1 g of the film was cut into small pieces. The cut films were mixed with 2 ml of methanol and vortexed for 3 minutes and then kept at room temperature for 3 hours. After these steps, the solution was centrifuged (2300 rpm) for 10 minutes. The obtained supernatant was used to evaluate the activity of DPPH radical trapping. 500 μ l of supernatant was mixed with 2 mL DPPH (0.06 mM) and vortexed again for 1 min and finally placed in a dark place at 25°C for 30 min. To evaluate the antioxidant activity, the absorbance of the samples was recorded at 517 nm using a spectrophotometer (Pharmacia

model, USA). For studying control sample absorbance, 2 ml of methanol, 2 ml of DPPH (0.06 mM) was added to 500 µl of methanol and its absorbance was read at 517 nm. Percentage of antioxidant activity was calculated using the following Equation (Siripatrawan & Harte, 2010).

$$\text{Antioxidant activity(\%)} = \frac{1 - A_{\text{sample}}}{A_{\text{control}}} \times 100$$

6

2.3.7. Electrical properties

A multimeter (VICTOR, 86D) was used to measure the electrical conductivity. For this purpose, the electrodes were connected to both ends of the film at a distance of 1 cm. After 30 seconds, the values of the electrical resistance were recorded.

2.3.8. Scanning electron microscopy (SEM)

Scanning electron microscopy method was used to study the morphology and surface structure of the prepared films. For this purpose, the SEM device with KYKY-EM3200 model was used. To image the surface of the films, film samples were glued to the base of the device and coated with gold particles. Then the surface of the films was photographed with different magnifications.

2.3.9. Fourier transform infrared (FTIR)

FTIR device (Shimadzu, Japan) was used to study the FTIR spectra of polylactic acid film and its composites. For this purpose, very small amounts of the film were mixed with potassium bromide in a ratio of 1 to 100. The prepared mixture was uniformly pulverized and pressed into 100 µm thick tablets. The prepared tablets were placed in the sample cell of the device and FTIR spectra were recorded in the range of 500 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹.

2.3.10. X-ray diffraction (XRD)

The X-ray diffraction method was used to study the crystalline-amorphous structure of the prepared films. For this purpose, XRD model MPD-B.V made in the Netherlands was used. The film samples were compressed on special disks for the XRD device and placed in the sample holder on the device. The X-ray of the device was 0.154 nm generated by CuK filtered with nickel. The reflected rays from the sample were recorded in the device in the range of angles 2θ = 2 to 60 degrees. The resulting curve was reported as the peak intensity curve against the reflectance angles of the sample (2θ).

2.3.11. Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)

TGA and DTA spectroscopy were used to study the thermal stability of polylactic acid film and the effect of nanoparticles and polyaniline on thermal stability. Thermal analysis device (Linseis, STE-PT-1000, and Germany) was used for this purpose. Samples were prepared first. The film samples were cooled in an

oven at 60°C for 1 hour to completely remove volatiles. The samples were then placed in the cell tube of the device and heated from 5 to 500°C at a rate of 10°C/min and TGA and DTA spectra were recorded.

2.3.12. Antibacterial properties

To evaluate the antimicrobial properties of the films, direct contact method was used on the microorganisms of *Escherichia coli* Gram-negative (ATCC 13706) and *Staphylococcus aureus* Gram-positive (ATCC 6538). For this purpose, film samples with a diameter of 0.5 cm were first prepared under sterile conditions and placed on Müller Hinton agar (Merck, Germany) containing 10⁶ bacteria. After that, all plates were incubated for 24 hours at 37 °C. After incubation, the growth rate of bacteria was evaluated. To ensure uniform growth of bacteria on the plate surfaces, a culture plate without film was considered for each of the tested bacteria. A bacterial plate was also used to ensure that the culture media was not contaminated (Ojagh et al., 2010).

2.4. Packaging of orange juice with polylactic acid active film

Oranges (Olinda Valencia variety) were prepared from the market (Urmia, Iran) and the orange juice was extracted by a semi-industrial orange juice extractor. The obtained orange juice was immediately packed in glass containers after passing through 1 mm mesh filters. For this purpose, glass container was sterilized and its wall was covered with PLA films and 100 ml of fresh orange juice was poured into the glass containers. The glass containing orange juice were closed with PLA films and completely sealed with a special glue. The samples were then stored in the refrigerator at 4°C. The physicochemical and microbial properties of samples were evaluated and at 0, 7, 28 and 56 days. The electrical properties of packaging films were also measured during storage time (Fig. 1-B).

Figure 1

2.5. Chemical and microbial properties of orange juice

2.5.1. pH measurement

To measure pH, first the pH meter was calibrated using standard buffers. The pH was then measured by directly inserting the electrode of the pH meter (Titro Line easy, Schott, UK) into the orange juice samples.

2.5.2. Measuring the amount of ascorbic acid

Iodine titration method was used to measure the amount of ascorbic acid. In this method, first, 20 ml of orange juice was mixed with 150 ml of distilled water. After adding one milliliter of 1% starch index solution, the resulting solution was titrated using iodine solution until a black blue color appeared. The amount of mg of ascorbic acid in 100 ml of the sample was calculated based on the following Equation (Kashyap & Gautam, 2012).

$$\text{mg of ascorbic acid in 100 ml of sample} = 0.88 \times \text{consumption reagent volume}$$

To prepare the iodine solution, 5 g of potassium iodide and 0.268 g of potassium iodate were dissolved in 500 ml distilled water and then 30 ml of sulfuric acid 3 Mo was added to it.

2.5.3. Browning index

Meydav et al. (1977) method was used to determine the browning index of orange juice. In this way, first 10 ml of orange juice were centrifuged (D 78532, Hettich, Germany) for 10 minutes at 4°C. Then 5 ml of the supernatant solution was mixed with 5 ml of ethanol (95%) and centrifuged again under similar conditions. Finally, the absorbance of the supernatant was recorded at 420 nm using a spectrophotometer (Pharmacia model, USA) as browning index (Meydav et al., 1977).

2.5.4. Microbial count of orange juice

At first, orange juice was diluted using Ringer's solution. For this purpose 1 ml of orange juice was transferred to a test tube containing 9 ml of Ringer's solution. The rest of the dilutions were prepared in the same way. PDA (Liofilchem, Italy) culture medium was used to count yeast-mold and the plates were incubated for 5 days at 25°C. The aerobic mesophilic bacteria were counted by mixed culture (pour plate) method using the PCA medium at incubation temperature of 35°C for 72 hours (Liofilchem, Italy). To measure acidophilus bacteria, OSA culture medium (Q-LAB, Canada) was used by pouring plate method and the plates were incubated for 48 hours. The tests were performed at 0, 28, 56 and 56 days in 4 replications and the results were reported as CFU/ml (Emamifar et al., 2010).

2.6. Statistical analysis

Statistical analysis of this study was performed in three parts. In the first part to investigate the effect of copper oxide, zinc oxide and polyaniline nanoparticles on the physicochemical properties of the film, the central composite design (Table 1-A) was used. Design Expert-10 software was used to design statistical design, data analysis and comparison of means (at 95% probability level). In the second part, a factorial design was used to investigate the effect of copper oxide, zinc oxide and polyaniline nanoparticles on structural, chemical and antibacterial properties (Table 1-B). The data in this section were done with three replications and Mini-Tab-17 software was used to analyze the data. In the third part, a factorial design was used to investigate the effect of the type of polymer used for packaging and the storage time of orange juice on the chemical properties of orange juice and the electrical properties of packaging films (Table 1-C). The data in this section were done with three replications and Minitab-17 software was used to analyze the data.

3. Results And Discussion

3.1. Response surface method

One of the design concepts of experiments is the response surface method (RSM). This method is useful for analyzing experiments in which one or more independent variables (as responses) are affected by

many variables and the goal is to optimize the response. One of the advantages of using this method and Design Expert software, in addition to reducing the number of experiments, is the possibility of providing a mathematical relationship between the independent variable and the dependent variables. In addition, in this method, in addition to numerical variables, it is possible to study the effect of qualitative variables. In this study, the response surface statistical method was used to investigate the effect of copper oxide, zinc oxide and polyaniline nanoparticles on the physicochemical properties of the film. Using the response surface method, three-dimensional curves and mathematical relationships between the independent variables in the film (copper oxide nanoparticles, zinc oxide and polyaniline) and the physicochemical properties of the film was analyzed. Table 2 shows the mathematical relationships and regression coefficients and the adjusted regression coefficients between the independent variables and the answers obtained.

Table 2

Mathematical models and regression coefficients between independent and dependent variables

Response	Equation	R ²	AdjR ²
Thickness (µm)	$= 0.1592 + 0.0186 * ZnO + 0.0269 * CuO - 0.005 * ZnO * CuO$	0.93	0.90
Water uptake (%)	$= 2.6194 - 0.3977 * ZnO + 0.0488 * CuO$	0.88	0.85
Moisture content (%)	$= 12.1936 - 1.26092 * ZnO - 1.12203 * CuO + 0.2044 * ZnO * CuO + 0.2980 * ZnO^2 + 0.3536 * CuO^2$	0.84	0.75
Solubility (%)	$= 7.50897 - 0.4666 * ZnO - 0.43111 * CuO$	0.91	0.90
WVP	$= 2.4691e-06 - 4.6533e-07 * ZnO - 4.1545e-07 * CuO + 1.1772e-07 * ZnO * CuO - 3.2409e-08 * ZnO^2 - 4.2794e-08 * CuO^2$	0.99	0.98
Antioxidant activity (%)	$= 16.4711 + 3.3394 * ZnO + 3.4327 * CuO - 0.94333 * ZnO * CuO$	0.92	0.89
Electrical resistance (MΩ)	$= 8456.95 + 8155.52 * ZnO + 7786.63 * CuO - 1655.56 * ZnO * CuO - 1739.62 * ZnO^2 - 2290.73 * CuO^2$	0.88	0.85

3-2- Thickness, WU, MC, water solubility and WVP

One of the most important problems in using biodegradable polymers in food packaging, especially watery food products (such as juices and concentrates), is the high sensitivity of biodegradable polymers to water. Most of these biodegradable polymers lose their mechanical and physical properties in the presence of water molecules. Polylactic acid is one of the few biodegradable polymers that has a very good waterproof property that makes this polymer suitable for use in the packaging of food products. The thickness of the packaging films is one of the factors that affect other film properties such as water absorption, moisture content, water solubility, water vapor permeability and mechanical properties, so check and control this factor in films is important. The aqueous properties of packaging films affect the

ability of these films to package food products. Many food products are affected by microbial and bacterial spoilage in wet conditions. If the packaging film has a high solubility in water (such as gelatin films and carboxymethylcellulose films), they will not be useful in the packaging of watery food products such as juices because they will dissolve and disappear in the food product. The packaging film must effectively control the penetration of water vapor into the packaging of moisture-sensitive foods to minimize microbial spoilage.

Figure 2 shows the effect of the amount of copper oxide and zinc oxide nanoparticles on the thickness and aqueous properties of polylactic acid/polyaniline films. As it is known, the addition of copper oxide and zinc oxide nanoparticles has a significant effect on increasing the film thickness and the highest thickness is related to the film contains 3% copper oxide and 3% zinc oxide. The increase in thickness in the presence of nanoparticles is due to the fact that these particles increase the solid matter in the film and lead to an increase in the thickness of the film. Among the aqueous properties of polylactic acid/polyaniline films, water vapor permeability is reduced in the presence of both copper oxide and zinc oxide nanoparticles, which is probably due to the fact that these nanoparticles reduce the voids between polymer chains. Therefore, water vapor molecules take up more space to pass through the film and the permeability to water vapor is reduced. Copper oxide and zinc oxide nanoparticles also reduce solubility, moisture content and moisture absorption. Moisture absorption of polylactic acid films (due to the hydrophobic nature of this polymer) is probably due to the presence of possible pores in the surface and width of the film that cause water molecules to penetrate into these voids. However, with the addition of copper oxide and zinc oxide nanoparticles to the film, the pores are filled and water molecules will not be able to penetrate in the film structure. In 2020, Asadi and Pirsā made a polylactic acid film modified with lycopene pigment and titanium oxide nanoparticles and studied its thickness and aqueous properties. The results of their research are in good agreement with the results of the present studies (Asadi & Pirsā, 2020). In 2012, Delpouve et al. investigated the water vapor barrier properties of polylactic acid films. Their research results confirm the results of the present study (Delpouve et al., 2012).

Figure 2

3.3. Antioxidant and electrical properties

The antioxidant properties are one of the most important properties of active films that are considered in the packaging of oxidation-sensitive food products. Active antioxidant films can easily increase the shelf life of food products such as oils by absorbing oxidizing agents. Antioxidants such as essential oils and metal oxide nanoparticles by contact with oxidizing agents quench them and protect the food from the oxidation process.

Figure 3 shows the effect of the amount of copper oxide and zinc oxide nanoparticles on the antioxidant properties and electrical resistance of polylactic acid/polyaniline films. As it is known, both copper oxide and zinc oxide nanoparticles have greatly increased the antioxidant properties of the film, and in films where copper and zinc oxide nanoparticles are present simultaneously, these two nanoparticles have a synergistic effect and the highest antioxidant property are observed. The antioxidant properties of various

nanoparticles such as titanium oxide, copper oxide and zinc oxide have been confirmed by various researchers. The antioxidant properties are investigated as the ability to absorb DPPH free radicals. The adsorption of these free radicals occurs either through oxidation/reduction or electrostatic reactions by antioxidant agents or these radicals are physically adsorbed on the agents. In the case of copper oxide and zinc oxide nanoparticles, it can be said that the deactivation of free radicals can be due to both electrostatic interactions between nanoparticles and DPPH radicals and can occur due to the physical adsorption of free radicals on the surface of nanoparticles. Das et al. (2013) investigated the antioxidant properties of metal oxide (copper oxide) nanoparticles. The results of their research confirm the results of this research (Das et al., 2013).

Electric conductive films can be used as smart films in food packaging. The electrical conductivity of these films changes in contact with chemical gases produced in the food product or due to mechanical pressure created in the food product. By observing the changes in electrical conductivity and making the relationship between storage conditions (temperature and storage time), chemical properties of the food and the electrical properties of the conductive film, mathematical models can be obtained. These mathematical models can help to detect the shelf life, expiration date and chemical conditions of the product. The primary electrical properties of conductive films can affect the sensitivity of these films to environmental changes. Therefore, it is very important to study the initial electrical properties of these films. The pure polylactic acid film had no electrical conductivity while polylactic acid/polyaniline/copper oxide/zinc oxide film had a good electrical conductivity (500 k Ω) which showed polyaniline induced a very good electrical property of the film. As can be seen from the curves of the effect of copper oxide and zinc oxide nanoparticles on the electrical resistance of films, these nanoparticles did not have a significant effect on the electrical property of the film, which indicates that by placing polyaniline between polylactic acid chains, significant electrical conductivity is created in the film that the placement of copper oxide and zinc oxide nanoparticles on polyaniline nanoparticles does not prevent the transfer of electrical charges. Electrical conductivity in conductive polymers, such as polyaniline, is due to the mobile carriers that are obtained by π electronic system. By removing electrons from the valence band (positive charge), or by adding electrons to the conduction band (negative charge), an electric charge is induced in the polymer chain and causes an important change in the position of the atoms at the charge site that finally changes electrical conductivity. In 2018, Pirsá et al. used polypyrrole to produce smart electrical conductive films based on bacterial cellulose film. They confirmed the establishment of good electrical conductivity in biodegradable films in the presence of polypyrrole. The results of their research are completely consistent with the results of the present study (Pirsá et al., 2018).

Figure 3

3.4. SEM and FTIR

Figure 4 shows the SEM images and FTIR spectra of polylactic acid films and their composites with polyaniline, copper oxide and zinc oxide. As can be seen from the SEM images, the pure polylactic acid film has a smooth surface with surface cracks in some places. In the polylactic acid/polyaniline composite film, the presence of polyaniline grains on the polymer surface in the dimensions of 50 to 120

nm is observed. In this film, the polyaniline beads are interconnected like rosary beads. The presence of polyaniline on the surface of polylactic acid can affect the thickness, water vapor permeability, and mechanical properties. The surface morphology of PLA/PAn/CuO, PLA/PAn/ZnO and PLA/PAn/CuO/ZnO films are very similar. In these films, the dispersion of copper oxide and zinc oxide particles in the dimensions of 20 to 50 nm on polyaniline beads is clear. PLA/PAn/CuO films have a more regular structure PLA/PAn/ZnO and PLA/PAn/CuO/ZnO, which is probably due to the fact that copper oxide has a more regular structure than zinc oxide. Wang et al. (2020) investigated the structure of polylactic acid film and its composites with polyaniline. The results of the present study are consistent with the results of Wang et al in terms of surface morphology and SEM images (Wang et al., 2020b). Tang et al. (2020) investigated the structure of polylactic acid film and its composites with zinc oxide nanoparticles. The results of Tang et al. in terms of surface morphology and dispersion of nanoparticles on the polymer surface confirm the results of the present study (Tang et al., 2020).

To study the chemical structure of the prepared films, their FTIR spectra were studied. In the pure polylactic acid spectrum, the peak of 3494 is related to the tensile vibration of the -OH groups. Peak at 2931 is related to interatomic vibrations in the R-CO-OH and C = C-OH groups. Peak at 2082 is related to C = O vibrations. Peak at 1719 is related to the vibrations of the acidic functional groups (RCOOH). Peak at 1453 shows the tensile vibrations of the CH₃ and CH₂ groups. The high peak at 1052 also confirms the C-O tensile vibrations in acidic groups. Peak at 753 also shows off-screen C-H vibrations. In the spectra of polylactic acid composite films with polyaniline, copper oxide and zinc oxide, all peaks related to the spectrum of pure polylactic acid are observed, with the difference that the peaks belonging to different functional groups shift to different wave numbers and some new peaks have been generated in these spectra, indicating that electrostatic interactions between polylactic acid, polyaniline, copper oxide, and zinc oxide have been established. These changes also confirm the presence of polyaniline, copper oxide and zinc oxide in the structure of the polylactic acid film. For example, peak at 3494 (corresponding to -OH vibrations) in the polylactic acid/polyaniline spectrum shifted to 3436 (corresponding to -OH and -NH vibrations). This almost extreme shift indicates that polyaniline strongly affects the chemical structure of polylactic acid. Also in the polylactic acid/polyaniline spectrum, a new peak is created in the 1478 cm⁻¹, which is related to N-O vibrations, which indicates the interaction between N related to polyaniline and O related to polylactic acid. Also on this spectrum, peak at 681 is related to RNH₂ and R₂NH vibrations. In the polylactic acid/polyaniline/copper oxide spectrum, the peak intensities of the OH and NH vibrations (at 3435 cm⁻¹) are significantly reduced, indicating that the CuO covers the OH and NH groups. In general, nanoparticles of copper oxide and zinc oxide significantly shifted the peaks belonging to the functional groups of polylactic acid/polyaniline composite film to different wavenumbers. These changes in the wavenumbers and the intensity of the corresponding peaks indicate the significant impact of these nanoparticles on the chemical structure of the polylactic acid/polyaniline composite film. Wong et al. (2020) investigated the structure of polylactic acid film and its composite with polyaniline using the FTIR spectrum. The results of their study on the peaks of the functional groups of polylactic acid and polyaniline confirm the results of the present study (Wong et al., 2020). Therias et al. investigated the effect of zinc oxide nanoparticles on the FTIR spectrum of polylactic acid and reported that the

nanoparticles had a significant effect on the wave number and peak intensities of the polylactic acid functional groups. The results of the FTIR spectra of the present study are in good agreement with the results of Therias et al. (Therias et al., 2012).

Figure 4

3.5. XRD, TGA and DTA

Figure 5 shows the XRD, TGA and DTA spectra of polylactic acid film and its composites. The XRD spectrum of pure polylactic acid film shows a wide peak at 2θ of 18 to 20 degrees, indicating the amorphous structure of polylactic acid film. In the spectrum of polylactic acid/polyaniline films, three sharp and well-defined peaks are observed in 2θ of 15, 20 and 25 degrees. These three sharp peaks are mounted on a wide peak corresponding to polylactic acid. Sharp peaks are related to the presence of polyaniline in the film structure. These three peaks also indicate that polyaniline (in the form of emeraldine) has a crystalline structure and these peaks correspond to crystal plates 113, 121 and 322, respectively. In the spectra of polylactic acid/polyaniline/copper oxide, polylactic acid/polyaniline/zinc oxide and polylactic acid/polyaniline/copper oxide/zinc oxide, the wide peak corresponds to the amorphous structure of polylactic acid has been disappeared and peaks related to the crystalline structure of polyaniline, copper oxide and zinc oxide are clearly visible. Peaks related to copper oxide are seen in 2θ of 32, 36, 38, 44 and 48 degrees, which indicates the presence of copper oxide nanoparticles in the structure of composite films. Peaks related to zinc oxide can be seen in 2θ of 32, 37, 42, 53, 63 and 65 degrees, which confirms the presence of crystalline zinc oxide nanoparticles in the structure of composite films (Ahmad, 2019). Almost all peaks related to polyaniline, copper oxide and zinc oxide can be clearly seen in the polylactic acid/polyaniline/copper oxide/zinc composite film. This film shows the highest number of peaks. The general conclusion of XRD spectra is that polyaniline, copper oxide and oxide have improved polylactic acid crystalline structure. Padmapriya et al. (2018) studied the structure of polyaniline by XRD spectrum. They report that polyaniline has a crystalline/semi-crystalline structure, which confirms the results of the present study (Padmapriya et al., 2018). de Souza et al. (2018) investigated the structure of polyaniline-copper oxide by XRD technique. The results of their report confirm the results of the present study in terms of peaks appearing for copper oxide and polyaniline-copper oxide composites (de Souza et al., 2018).

Examination of the TGA spectra of all films shows that in all films the thermal decomposition of the film occurs in two stages. The first stage of film decomposition occurs at a temperature of approximately 70 to 150°C. The rate of thermal decomposition of the films in the first stage is 5 to 10% of the film weight. The thermal decomposition of the first stage is probably due to the evaporation of chloroform molecules trapped in the film structure because chloroform is used as a solvent for lactic acid monomers in the film preparation stage. Also, the thermal decomposition of the first stage can be due to evaporation or thermal decomposition of thermally unstable materials in the film structure. The second stage of thermal decomposition occurs at a temperature of 200 to 350°C. The second stage of thermal decomposition is related to the structural decomposition of polylactic acid and polyaniline films. By comparing different composites, it was found that the polylactic acid/polyaniline composite film (decomposition at 344) has

higher thermal stability than the pure polylactic acid film (decomposition at 269). The reason for the higher stability of polylactic acid/polyaniline composite films than pure polylactic acid films is due to this fact that strong interactions between polyaniline and polylactic acid occur during polyaniline synthesis.

Examination of TGA and DTA results also showed that the addition of copper oxide and zinc oxide nanoparticles to the polylactic acid/polyaniline composite reduced the thermal stability, which is probably due to the fact that copper oxide and zinc oxide nanoparticles are located between polylactic acid-polyaniline polymer chains and reduce the electrostatic interactions between the polymer chains and thus reduce the thermal resistance. Therefore, polylactic acid/polyaniline film, which simultaneously contains copper oxide and zinc oxide nanoparticles, has the lowest thermal stability compared to polylactic acid/polyaniline film, which shows the synergistic effect of copper oxide and zinc oxide nanoparticles in reducing thermal resistance of film. Also, by examining the percentage of film decomposition in the second stage, it was observed that by adding copper oxide and zinc oxide nanoparticles to the film, the amount of thermal decomposition of the film is reduced. Given that the nanoparticles of copper oxide and zinc oxide have very high decomposition temperatures, this result is acceptable and logical. Wang et al. (2020) investigated the effect of polyaniline on the thermal stability of polylactic acid films using TGA spectroscopy. They reported that polyaniline increases the thermal stability of polylactic acid, which confirms the results of the present study (Wang et al., 2020b). Marra et al. (2017) investigated the effect of titanium oxide and zinc oxide nanoparticles on the thermal resistance of polylactic acid. They concluded that the nanoparticles somewhat reduce the thermal stability of the film. The results of Marra et al. (2017) confirm the results of the present study (Marra et al., 2017).

Figure 5

3.6. Antibacterial properties

Antibacterial active films used in food packaging delay food spoilage by inhibiting bacterial growth and increase food shelf life. Figure 6 shows the growth inhibition zone of two types of bacteria, Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) in the presence of polylactic acid film and its composites. As it turns out, the pure polylactic acid film does not have any specific antibacterial properties against any of the bacteria. The addition of all three materials polyaniline, copper oxide and zinc oxide have created antibacterial properties in the polylactic acid film. The highest halo of non-growth is observed in the polylactic acid film containing all three substances polyaniline, copper oxide and zinc oxide, which shows that these three substances have strengthened the effect of each other. Also, the antibacterial properties of films containing polyaniline, copper oxide and zinc oxide against Gram-positive bacteria (*Staphylococcus aureus*) were higher than Gram-negative bacteria (*Escherichia coli*), which is due to the structure of the bacterial cell wall. The physical and chemical structure of Gram-negative bacteria are more complex, and antibacterial agents are less able to penetrate into the cells of Gram-negative bacteria and therefore have less ability to inactivate them. Gram-positive bacteria, on the other hand, have a simpler cell wall and antibacterial agents easily penetrate and inactivate the bacteria. Compared to Gram-positive bacteria, Gram-negative bacteria are more resistant to antibiotics because of their impermeable wall. The antibacterial property of polyaniline is probably due to

the fact that the surface of polyaniline is filled with positive and negative electric charges as well as electrical cavities, which can establish electrostatic interactions with the relative electric charge of the bacterial surface and disrupt bacterial activity. Kucekova et al. (2014) investigated and confirmed the antibacterial properties of polyaniline. Their research results confirm the results of the present study (Kucekova et al., 2014). Widiarti et al. (2017) synthesized ZnO-CuO nanoparticles and investigated their antimicrobial properties. Their research results confirm the results of the present study (Widiarti et al., 2017).

Figure 6

3.7. Active and smart packaging of orange juice with polylactic acid film

3.7.1. The effect of active film on chemical quality control of orange juice

Figure 7 shows the chemical factors (pH, ascorbic acid and browning index) of orange juice packaged with polylactic acid films during 56 days of storage. As can be seen from the curves, the pH of orange juice (packaged with all 5 types of polymers) increased relative during storage. The increase in pH is probably due to the growth of aerobic mesophilic microorganisms and the degradation of vitamin C during storage. The highest pH changes are related to the sample packaged with pure PLA and the lowest pH changes are related to the sample packed with PLA/PAn/CuO/ZnO. This result shows that nanoparticles of copper oxide, zinc oxide and polyaniline have caused the chemical stability of orange juice. In other words, nanoparticles of copper oxide, zinc oxide and polyaniline have controlled the factors that produce OH⁻ ions during storage. Usually the amount of ascorbic acid in orange juice is in the range of 26–84 mg/100 g of extract (Plaza et al., 2006). In the case of ascorbic acid, the amount of ascorbic acid decreases with increasing storage time, which reduces the nutritional value of the juice. The reason for the decrease in ascorbic acid during storage is probably related to the oxidation process of this acid. Also, by examining ascorbic acid curve, it was found that the type of polymer used for packaging does not have a significant effect on the stability of ascorbic acid. By studying the effect of polyethylene bags on the shelf life of orange juice, Fellers reported that the decrease in ascorbic acid of orange juice was due to oxidation reactions during storage (Fellers, 1998).

Food browning is the process by which a food turns brown during a series of chemical reactions. The pathways involved in the browning process are specifically divided into two main categories: the enzymatic and non-enzymatic browning pathways. Enzymatic browning is one of the most important reactions that occurs in most fruits, vegetables as well as seafood. These processes affect the taste, color and value of these foods. In general, this type of browning is a chemical reaction between a polyphenol oxidase, catechol oxidase, and other enzymes that converts natural phenols to melanin and benzoquinone. Performing the process of enzymatic browning (also called food oxidation) requires available oxygen. This process begins with the oxidation of phenols by the enzyme polyphenol oxidase to

quinone. Due to its high nucleophilic nature, quinone has a great potential for accepting protein. The quinones produced then participate in a series of polymer reactions, eventually leading to the formation of brown pigments on the surface of the food. In non-enzymatic browning, as in the case of enzymatic browning, a brown pigment is produced in the food. The two main forms of non-enzymatic browning are caramelization and Maillard reaction. The rate of both reactions is a function of the amount of water in the sample. By studying the browning index curve, it was found that in all 5 types of packaging, browning has increased with increasing storage time of orange juice. However, the increase in browning index in PLA/PAn/CuO/ZnO packaging is less than other packages. The highest increase in browning index during storage time is related to pure PLA packaging. As mentioned, enzymatic browning is an oxidation chemical reaction and since in PLA/PAn/CuO/ZnO polymer, all three nanoparticles of copper oxide, zinc oxide and polyaniline have antioxidant properties, so PLA/PAn/CuO/ZnO with the highest antioxidant properties has reduced the oxidation process and reduced the browning speed of orange juice. In general, by examining the chemical properties of orange juice packaged with various polylactic acid composites, it was found that the highest quality control occurred in orange juice packed with PLA/PAn/CuO/ZnO. In a similar study, Kumar et al. (2019) used ZnO-modified agar active film in green grape packaging. They showed that the use of antioxidant active film controls the chemical quality of the product, the results of which confirm the results of the present study (Kumar et al., 2019). Polat et al. (2018) prepared polypropylene film containing various nanoparticles and used it for packaging and quality control of lemon juice. Their results showed that the active film controls the chemical quality of fruit juice, which confirms the results of the present study (Polat et al., 2018).

Figure 7

3.7.2. The effect of active film on microbial quality control of orange juice

Figure 8 shows the microbial factors (yeast-mold, total aerobic bacteria and acidophilus bacteria) of orange juice packed with polylactic acid films during 56 days of storage. Examination of the yeast-mold curve showed that the type of polymer used for packaging did not have a significant effect on yeast-mold. Molds and yeasts were more compatible with orange juice and cold storage conditions than bacteria. This result was consistent with the studies of Emamifar et al (Emamifar et al., 2010). However, by examining the curves of total aerobic bacteria and acidophilus bacteria, it has been determined that with increasing storage time, the levels of total aerobic bacteria and acidophilus bacteria increase. Examining the effect of polymer type on the growth of total aerobic bacteria and acidophilus bacteria, it was found that the growth rate of total aerobic bacteria and acidophilus bacteria in the presence of PLA/PAn/CuO/ZnO polymer is the lowest. This result indicates that the antibacterial nanoparticles of copper oxide and zinc oxide are highly effective in controlling the microbial quality of orange juice. Because polyaniline also has antibacterial properties, in PLA/PAn/CuO/ZnO film, polyaniline has a synergistic effect with copper oxide and zinc oxide nanoparticles and has shown the greatest effect in controlling the microbial quality of orange juice. Jin and Niemira (2011) used antibacterial modified polylactic acid film for packaging and microbial quality control of apples. They show that the active film

has the ability to control the growth of *Escherichia coli* and *Salmonella bacteria*. Their research results confirm the results of the present study (Jin & Niemira, 2011). Lee et al. (2004) investigated the effect of antimicrobial packaging on the rate of microbial spoilage of milk and orange juice. They have confirmed the effect of antibacterial packaging on microbial quality control of orange juice (Lee et al., 2004). Fernández et al. (2009) studied the antimicrobial effects of zinc oxide, copper oxide and magnesium oxide and reported that these three metal oxides have good antimicrobial power against a wide range of microorganisms. They have also reported that the reason for the antimicrobial effect of metal nanoparticles is the production of free radicals in the microbial environment and consequently damage to cell membranes and their eventual destruction (Fernández et al., 2009). Llorens et al. (2012) also investigated the antimicrobial properties of cellulose/copper oxide composites and concluded that copper oxide nanoparticles showed strong antifungal activity in pineapple juice; it reduced the load of mold and yeast up to 4 logarithmic cycles. However, it showed weaker antifungal activity in melon juice, which is probably related to the neutral pH of melon juice, which prevents the exchange of copper ions (Llorens et al., 2012). Ram et al. (2013) investigated the effect of packaging containing oxidized nanoparticles on the shelf life of fresh mandarin oranges. Packaging containing oxidized nanoparticles was suitable for maintaining the microbial quality during 6 to 30 days after packaging (Ram et al., 2013).

Figure 8

3.7.3. Ability of smart film in identifying the storage time of orange juice

The purpose of food packaging is to increase the shelf life of food by preventing bacterial spoilage or loss of nutrients. Smart and active packaging systems produced with nanotechnology will be able to respond to environmental conditions such as changes in temperature and humidity. Smart packaging systems are systems that can warn of product quality changes during storage. Smart packaging has sensors that determine the freshness of the material. Smart food packaging can detect that its contents are spoiling and alert the customer. As the process of food spoilage begins, this active packaging will release preservatives such as antimicrobials, condiments, dyes or supplements into the food. Figure 9 shows the calibration curve of the relationship between shelf life and changes in electrical resistance of polyaniline-containing films. In orange juice packaging, different gases are produced according to biological and chemical activities. These gases put pressure on the polymers used for packaging at the bottle cap. Due to the pressure caused by these gases, the electrical resistance of the film changes. Over time, the amount of gas produced increases, and naturally the pressure applied to the film increases and the rate of change in electrical resistance also increases. The results of the electrical resistance of the packaging films showed that there is a linear-exponential relationship between the changes in the electrical resistance of the film and the storage time of orange juice. By examining the electrical resistance of the film in each day of storage, it is possible to estimate the storage time of orange juice and the exact expiration time of orange juice. By comparing the sensitivity of different films to storage time, it was found that PLA/PAn/ZnO film has the highest sensitivity to chemical changes during storage of orange juice. In a similar study, Pirsá and Shamusí used polypyrrole-modified bacterial cellulose film

for intelligent packaging of chicken thigh meat. They reported that there is a good linear relationship between storage time and temperature and changes in electrical resistance, which by examining this relationship the expiration date of chicken thighs meat can be estimated (Pirsa & Shamus, 2019). Asdagh and Pirsa (2020) used smart and active pectin/beta-carotene film to package local butter. They reported that active and intelligent film increased the durability of the local butter, also could estimate the corruption of local butter (Asdagh & Pirsa, 2020).

To evaluate the performance of smart films in identifying the shelf life of orange juice (expiration date), orange juice samples were prepared and packaged with 4 films and their electrical resistance was measured randomly on different days (real time). By placing the electrical resistance value in the mathematical models obtained in Fig. 9, the storage time was calculated (estimated time). From the following relationships, the error and accuracy of the films in calculating the storage time were calculated. The results verified the acceptable performance of smart films in determining the shelf life of two samples of orange juice (Table 3). The results of Table 3 show that all 4 types of smart films with an accuracy of over 90% are able to detect the storage time of orange juice.

Table 3

Error and accuracy of smart film performance in determining the shelf life of two samples of orange juice

Sample	Film type	Real storage time	Estimated storage time	Error of detection (%)	Accuracy of detection (%)
1	PLA/PAn	20	22	10	90
	PLA/PAn/CuO	20	21.5	7.5	92.5
	PLA/PAn/ZnO	20	21.8	9	91
	PLA/PAn/CuO/ZnO	20	21	5	95
2	PLA/PAn	45	42.5	5.5	94.5
	PLA/PAn/CuO	45	43.1	4.2	95.8
	PLA/PAn/ZnO	45	46.7	3.7	96.3
	PLA/PAn/CuO/ZnO	45	45.8	1.7	98.3

$$\text{Error of detection}(\%) = \frac{\text{Realtime} - \text{Estimatedtime}}{\text{Realtime}} \times 100$$

8

$$\text{Accuracy of storage time detection}(\%) = 100 - \text{Error of detection}$$

9

Figure 9

4. Conclusion

In this study, the biodegradable conductive film was prepared based on polylactic acid, modified with polyaniline, zinc oxide and copper oxide. Electricity conductive films were used for intelligent packaging of orange juice. Based on the results, the water vapor permeability of PLA film was reduced in the presence of both copper oxide and zinc oxide nanoparticles. Copper oxide and zinc oxide nanoparticles also reduced solubility, moisture content and moisture absorption. Both nanoparticles of copper oxide and zinc oxide greatly enhanced the antioxidant properties of the film. The pure polylactic acid film had no electrical conductivity while polylactic acid/polyaniline/copper/zinc oxide film had a good electrical conductivity (500 k Ω). According to the SEM images, the pure polylactic acid film had a smooth surface with surface cracks in some places. In the polylactic acid/polyaniline composite film, the presence of polyaniline grains on the polymer surface in the dimensions of 50 to 120 nm is observed. According to the FTIR results, copper oxide and zinc oxide nanoparticles have a significant effect on the chemical structure of polylactic acid/polyaniline composite films. The addition of all three materials polyaniline, copper oxide and zinc oxide caused antibacterial properties in the polylactic acid film. By examining the chemical and microbial properties of orange juice packaged with various polylactic acid composites, it was found that the active films control the chemical and microbial quality of orange juice. The results of the electrical resistance of the packaging films showed that there is a linear-exponential relationship between the changes in the electrical resistance of the film and the storage time of orange juice. By examining the electrical resistance of the film in each day of storage, it is possible to estimate the storage time and the expiration time of orange juice. The results showed that smart films with an accuracy of over 90% have the ability to detect the storage time of orange juice.

Declarations

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Author's contribution

Mahmoud Rezazadeh-Bari conceived of the presented idea. Parisa Abdolsattari developed the theory and performed the computations. Sajad Pirsā verified the analytical methods. Parisa Abdolsattari discussed the results and contributed to the final manuscript. Parisa Abdolsattari out the experiment. Sajad Pirsā wrote the manuscript and revised it.

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Data Availability Statement

The datasets generated during and/or analyzed during the current study are not publicly available, but are available from the corresponding author on reasonable request.

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Figures

Figure 1

Different PLA films and their composites (A) and active/intelligent packaging of orange juice with PLA films (B)

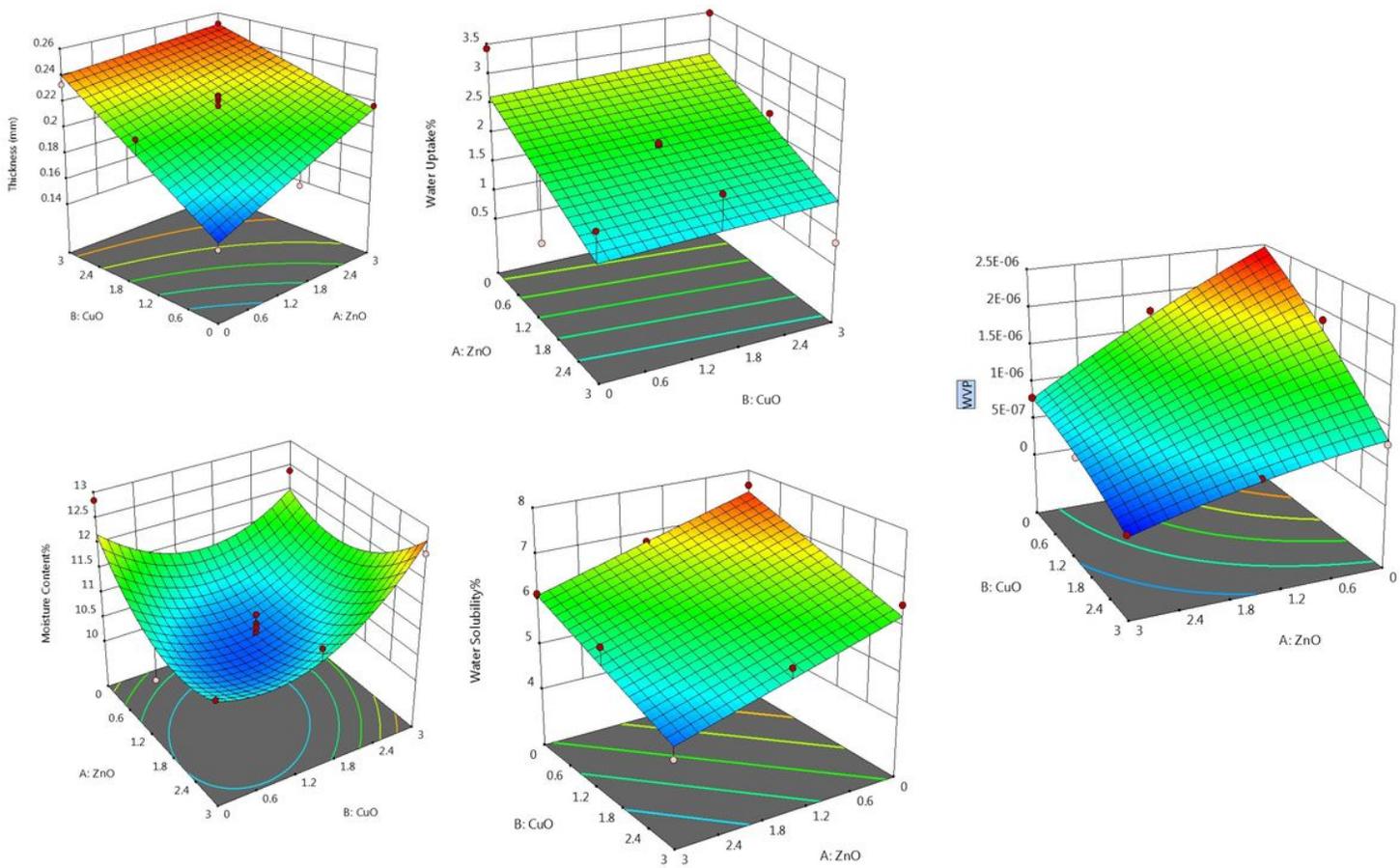


Figure 2

3-dimensional plot of effect of CuO and ZnO on the thickness and aqueous properties of poly(lactic acid)/polyaniline film

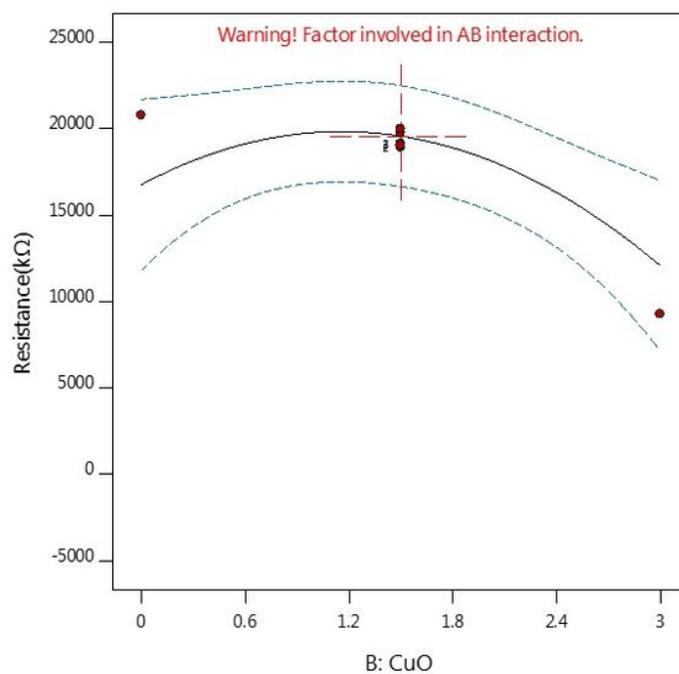
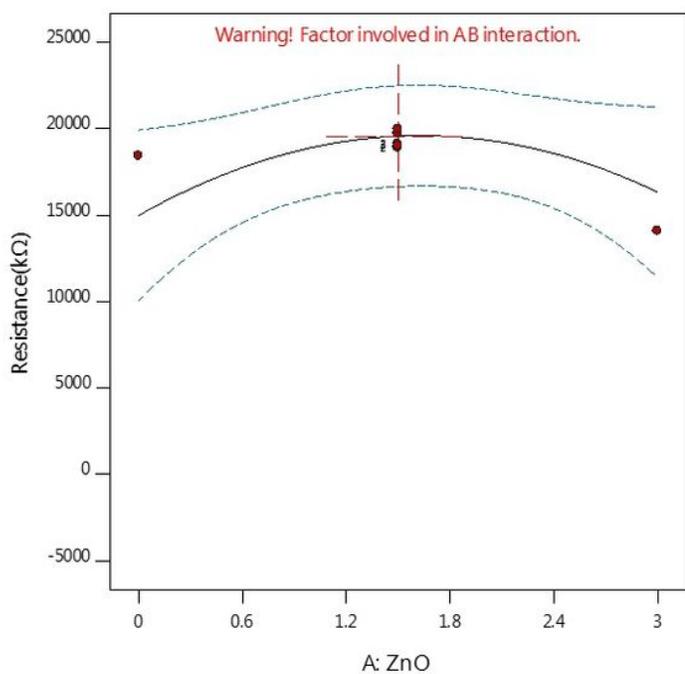
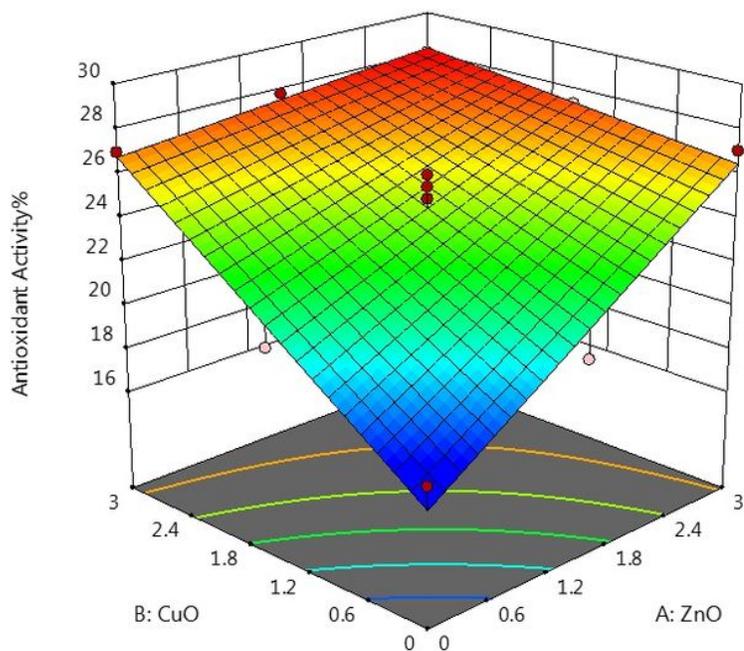


Figure 3

Effect of CuO and ZnO nanoparticles on antioxidant properties and electrical resistance of polylactic acid/polyaniline film

Figure 4

SEM (A) and FTIR (B) spectra of polylactic acid film and its composites

Figure 5

XRD (A), TGA and DTA (B) spectra of polylactic acid film and its composites

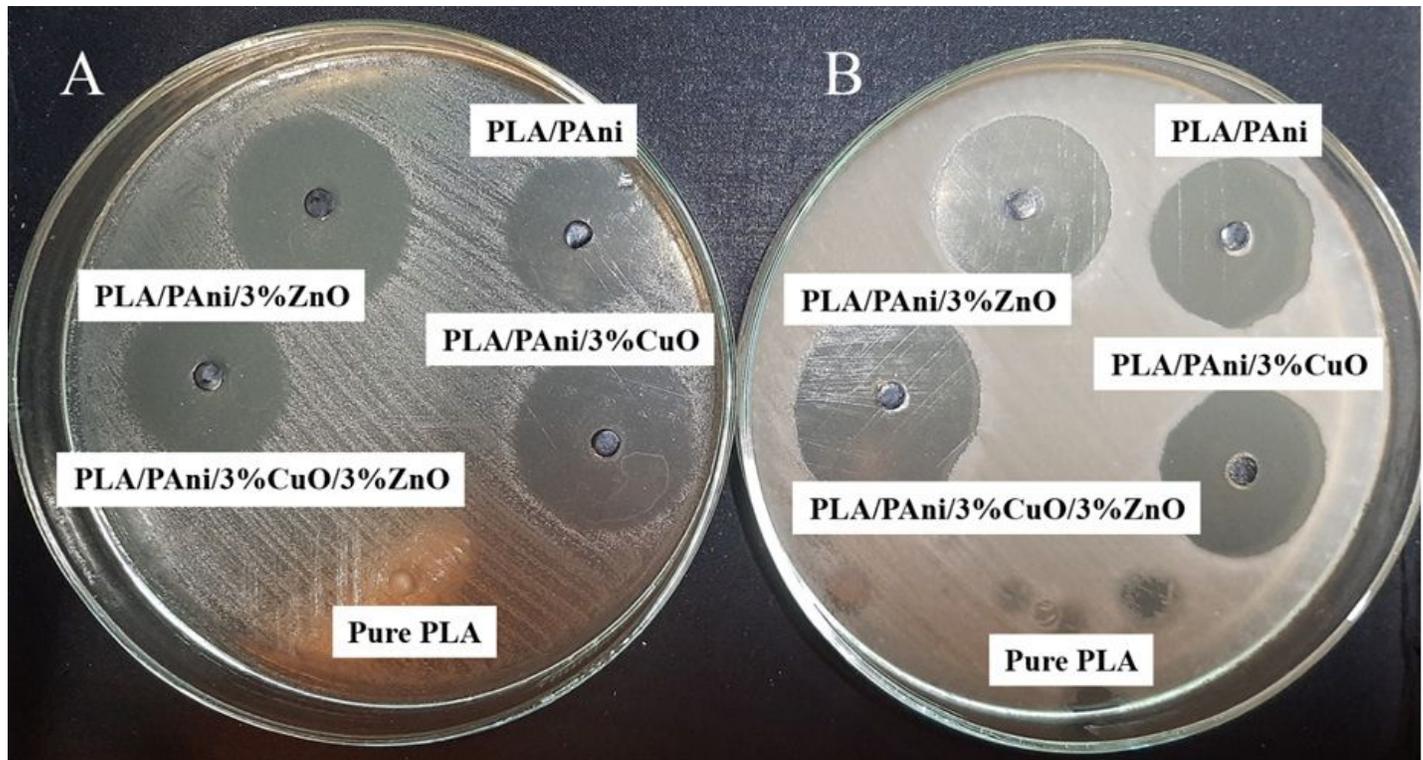


Figure 6

Non-growth halo of *Escherichia coli* (A) and *Staphylococcus aureus* (B) in the presence of polylactic acid films

Figure 7

Chemical factors (pH, ascorbic acid and browning index) of orange juice packaged with polylactic acid films during 56 days

Figure 8

Microbial factors (yeast-mold, total aerobic bacteria and acidophilic bacteria) of orange juice packaged with polylactic acid films during 56 days of storage

Figure 9

Calibration curve of the relationship between storage time and changes in electrical resistance of film