

Natural pigments-doped polymer films synthesis by solution casting method and characterization

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Recently, research and development activities in both public and private sectors have gained significant momentum due to the use of polymeric and polymer composite films in various fields, including packaging, optics, electronics, coatings, and solar cells. However, the increasing consumption of synthetic polymers makes a rise in plastic waste, causing adverse environmental impacts. To eliminate these effects, the use of biodegradable polymers has become increasingly important. In this study, polyvinyl alcohol (PVA) was selected as a biodegradable polymer matrix, and dye-doped polymer films were fabricated by doping natural pigments- lutein and β -carotene- at concentrations ranging from 3% to 5%. The produced films were characterized using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), tensile testing, scanning electron microscopy (SEM), and X-ray diffractometry (XRD). Tensile test results revealed that β -carotene enhanced the tensile strength of pure PVA films, whereas lutein combination resulted in a reduction in mechanical strength. DSC analysis indicated that the addition of both β -carotene and lutein increased the melting temperature of the PVA matrix. Polyvinyl alcohol, has been proven to be one of the polymers suitable for packaging materials and many other sectors in terms of production conditions, usability and biodegradability. The produced pure and dye-added films can be preferred as packaging materials due to their smooth surface and good durability.

Keywords: Polyvinyl alcohol; Biodegradable polymers; Natural pigments; Polymeric films; Packaging materials

INTRODUCTION:

Due to reasons such as the ever-increasing population, consumption habits and economy, non-biodegradable polymers are preferred and their consumption is increasing in many sectors. At this point, polymers that are completely biodegradable, do not harm the nature and do not create waste should be preferred and new studies should be carried out to solve the problems.

Polymers are long-chain, high molecular weight-compounds formed by the bonding of many equal or different atom groups with more or less regular chemical bonds and it have important application areas [1]. Polymeric structured films can consist of natural and artificial (synthetic) polymers. Layered polymeric structures up to 0.2-0.3 mm thickness are called plastic films or polymeric structured films. There is more than one method of producing films. Each method has its own parameters. The properties of the films to be produced should be determined according to their usage areas and the production method should be selected accordingly. For example, if consumed in the food industry, polymer structured films; carbon dioxide, oxygen etc. They are required to exhibit strong barrier properties

against gases and have the ability to come into contact with food. Methods such as extrusion, blow molding, coating, rotational molding, solution casting, double bubble processing, compression molding (pressure thermoforming) and vacuum thermoforming are applied to produce polymer structured films according to the desired properties [2]. Solution casting method is widely preferred due to its advantages such as being more economical than other methods in terms of cost and not requiring pressure. It is generally a process in which a liquid polymer is poured into an open mold or onto a surface and solidified by drying. It can be produced in different shapes such as round, square, tube and rod [3]. As a result, while the material takes the shape of the mold, a polymerization reaction takes place in the mold [4].

There are studies on polymer structured films in the literature. In one study, sustainable packaging materials were developed using biodegradable polymers, namely polylactide (PLA) and polyhydroxybutyrate (PHB), combined with natural colorants such as β -carotene, chlorophyll, curcumin, and lutein, which are widely utilized in the food industry. The incorporation of these pigments enabled the materials to exhibit pronounced color

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variations in response to different environmental conditions, thereby imparting smart packaging functionality by providing visual indications of product status and material lifespan [5]. In another investigation, the performance of starch-based biodegradable films was enhanced through polymer blending. Composite films were fabricated by incorporating different proportions of PVA (10%, 30%, 50%, 70%, and 90% relative to the starch content) into the starch matrix using the solvent-casting technique. The resulting films were comprehensively evaluated for their mechanical properties, barrier performance, water solubility, water contact angle, and biodegradation behavior. The findings demonstrated that starch-PVA composite films possess considerable potential as eco-friendly alternatives for food packaging applications [6]. In another study, hydrogel films based on polyvinyl alcohol (PVA) and tannic acid (TA) at various ratios were synthesized and the structure of the synthesized films was examined with characterization techniques such as FTIR, TGA, DSC, SEM, XRD and DTG. Synthesis of hydrogel films was achieved by first mixing TA and PVA and then pouring the solution into petri dishes and keeping it at 50 °C overnight. In the synthesis of PVA/TA hydrogel films, the films were kept in saturated salt solution for 6 hours to increase durability. As a result of the experiment, it was concluded that the mechanical strength of the films kept in saturated salt solution was better and adding TA to PVA-based films improved the thermal and hardness properties compared to pure PVA polymer [7]. In a separate study, low-cost laser cut-off filters were developed using poly(vinyl alcohol) (PVA)-based composite films containing carmine dye. Both pristine PVA films and carmine dye-incorporated PVA composite films were fabricated via a conventional solution-casting method. For the preparation of pure PVA films, approximately 22.5 g of PVA was dissolved in 1 L of distilled water under continuous magnetic stirring at 50 °C and 700 rpm for 24 h. Composite films were subsequently prepared by incorporating different concentrations of carmine dye into the PVA matrix, with dye contents ranging from 0.11 wt% to 27.27 wt%, following the same casting procedure. Characterization of the films cut into suitable dimensions demonstrated that the carmine dye/PVA composite films exhibited promising performance as laser cut-off filters, indicating their potential applicability in low-cost optical filtering systems. [8]. In this study, polymeric films were produced by mixing different amounts of glycerol, NaCaS

(Sodium caseinate) and polyethylene materials in the extruder under certain conditions. Then, the mechanical, thermal, contact angle, water vapor permeability, etc. properties of the produced films were determined, and characterization tests were carried out using SEM and FTIR analyses.

PVA is a polymer with high water retention and moisture retention capacity due to its high hydrophilic properties. Additionally, they are used in many industrial products thanks to their high adhesion and excellent film forming properties [10-12]. Lutein is a natural carotenoid pigment and is found in green leafy vegetables, yellow fruits and eggs. Lutein production generally involves two steps: plant extraction and refining. Plant extraction is carried out by extracting marigold flowers. Afterwards, the lutein extract is refined and made ready for use in various industries [13-15]. Beta-carotene is a type of carotenoid pigment and is an organic, strongly colored red-orange pigment found abundantly in mushrooms, plants and fruits. β -Carotene is a popular ingredient, especially used in nutritional supplements and cosmetic products. It is also popular as an ingredient used in food supplements and colorants [16-18].

In this study, 3 wt% pure PVA films, 3 wt% β -carotene-doped PVA films, and 3 wt% lutein-doped PVA films were produced using the solution casting method. The novelty of this study is the comprehensive evaluation of how lutein and β -carotene specifically affect the thermal, mechanical, chemical, and morphological properties of PVA films. To address the lack in the literature, the films were characterized using XRD, FTIR, SEM, DSC, and tensile testing. This study aims to assess the influence of these natural pigments on PVA films, highlighting their potential as sustainable and functional materials for the packaging industry and other industrial applications.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA) with a molecular weight of 89,000-98,000 was purchased from Interlab Laboratory Products Industry and Trade Inc. and stored at room temperature. Lutein and β -carotene were obtained from Ruber Biotechnology and Chemical Industry Tic. Ltd. and stored at -20 °C. Deionized water, used as the solvent, was produced using a Lauda-GFL pure water system (Gesellschaft für Labortechnik mbH).

Synthesis of pure PVA film

A 3 wt% PVA solution was prepared by accurately weighing the required amount of PVA

using a precision balance (Pioneer, OHAUS). The polymer was dissolved in deionized water in 50 mL beakers and continuously stirred at 500 rpm for 4 h at 85 °C until a clear homogeneous solution was obtained. Subsequently, the solution was cast into Petri dishes and dried in an oven at 40 °C for 48 h to produce PVA films.

Synthesis of dye-doped PVA films

Initially, a 3 wt% PVA solution was prepared by dissolving the polymer in 40 mL of deionized water under continuous stirring at 500 rpm for 4 h at 85 °C. In a separate step, β -carotene (3 wt%) was dispersed in 10 mL of deionized water and stirred at 500 rpm for 4 h at room temperature. The β -carotene dispersion was subsequently incorporated into the PVA solution and mixed for an additional 1 h at 500 rpm. To improve the homogeneity of the final formulation, the mixture was centrifuged at 4000 rpm for 15 min. The resulting solution was then cast into Petri dishes and dried at 40 °C for 48 h to obtain β -carotene-loaded PVA films. Following the same experimental protocol, including identical processing conditions and equipment, lutein-doped PVA films containing 3 wt% lutein were also fabricated. Figures 1a and 1b show the 3 wt% lutein-doped PVA and 3 wt% β -carotene-doped PVA films after the drying process, respectively.

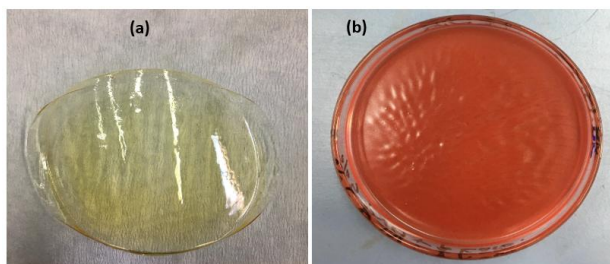


Figure 1. a) Lutein-doped PVA film; b) β -Carotene-doped PVA film

Characterization of pure and dye-doped PVA films

SEM analysis was employed to examine the surface morphology of the samples using a Zeiss EVO® LS 10 microscope at a magnification of 5000 $\times$. Crystalline characteristics were investigated by X-ray diffraction (XRD) using a PANalytical X'Pert Pro diffractometer, operating with Cu-K α radiation (45 kV, 40 mA). XRD measurements were performed by collecting diffraction patterns within a 2θ range of 5°–90° at a scanning rate of 2° min⁻¹. The chemical structures of the films were analyzed using FTIR on a Perkin Elmer Spectrum instrument equipped with an attenuated total reflectance (ATR) accessory, over the wavenumber range of 4000–400 cm⁻¹. Thermal properties were investigated by differential scanning calorimetry

(DSC) using a NETZSCH DSC 3500 calorimeter, where samples were heated from 30 °C to 210 °C at a constant rate of 30 K min⁻¹. Mechanical properties were assessed through tensile testing at ambient temperature using an Instron 5982 universal electromechanical testing machine. Films were prepared in dimensions of 15 mm $\times$ 40 mm and tested at a crosshead speed of 10 mm min⁻¹. The elongation at break and Young's modulus of the films were subsequently determined from the obtained stress-strain data.

RESULTS AND DISCUSSION

SEM analysis was performed to investigate the surface morphology and microstructure of pure and dye-doped PVA films. The effect of dye incorporation on the surface properties of the films was evaluated using SEM images. Figure 2 shows SEM images of 3 wt% (a) pure, (b) β -carotene-doped, and (c) lutein-doped PVA films at 5000 $\times$ magnification. The SEM images of all 3 wt% pure and dye-doped films revealed flat, smooth, and non-porous surfaces, indicating that the incorporation of the natural dyes did not significantly alter the surface morphology of the PVA films.

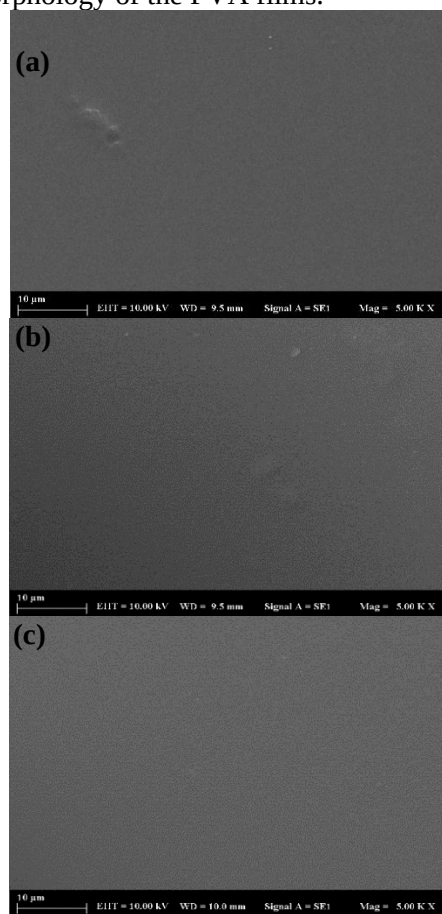


Figure 2. SEM images of 3 wt% a) pure b) β -carotene c) lutein doped PVA films at 5000X magnification.

Bonds and functional groups of the dye-doped polymeric films were characterized by FTIR analysis (Fig. 3). In the pure 3 wt% PVA polymeric film, the main peaks at 3260 cm^{-1} - 2940 cm^{-1} are associated with the stretching of the oxygen-containing functional group OH and CH. The peaks at 1657 cm^{-1} and 1562 cm^{-1} are C=O carbonyl group stretching and C=C stretching, respectively. Additionally, there are C-C stresses at wave frequencies of $1416.37 - 1328.58\text{ cm}^{-1}$. The functional groups of PVA $(\text{C}_2\text{H}_4\text{O})_x$ films detected are in line with the literature data [19]. When chemical bonds of 3 wt% β -carotene-doped PVA film are examined, the main peaks at 3257.894 cm^{-1} - 2909.505 cm^{-1} in the FTIR spectrum are attributed to OH and CH stretching, respectively. The 1655 cm^{-1} peak belongs to the C=O carbonyl group stretching, and the 1419.97 cm^{-1} - 1328.42 cm^{-1} peak belongs to the C-C stretching peaks. In the 3 wt% lutein-doped PVA films, the peaks in the bands 3266.727 cm^{-1} - 2937.814 cm^{-1} in the FTIR spectra are referred to OH and CH stretching, respectively. The frequency of 1659.188 cm^{-1} belongs to C=O carbonyl group stretching and 1416.453 cm^{-1} - 1327.985 cm^{-1} peaks belong to the C-C functional group. There are no C=C stretch peaks in dye-doped PVA films. In lutein- and β -carotene-loaded PVA samples, a slight broadening and small shifts in the O-H band may indicate weak hydrogen bonds or interactions formed by the loaded carotenoids with PVA. The slight increase in band intensity in the C-H bands (2850 - 2950 cm^{-1}) region with carotenoid loading was associated with the contribution of hydrophobic alkyl groups.

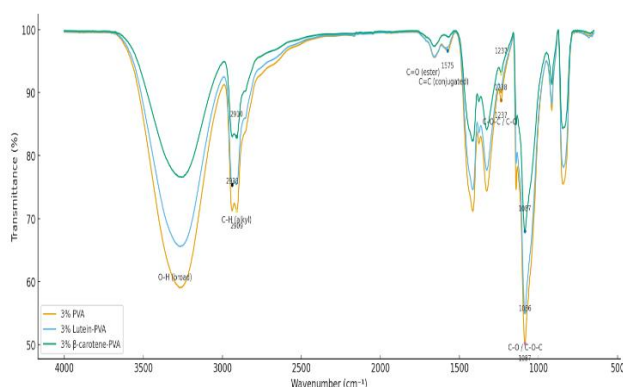


Figure 3. FTIR spectra of pure and dye-doped PVA films

X-ray diffraction (XRD) analysis was performed to investigate the crystal structure of the synthesized films. The XRD pattern of the 3 wt% pure PVA film exhibited a characteristic peak at $2\theta = 19.51^\circ$, which is attributed to intermolecular hydrogen bonding within the polymer matrix. This result is consistent

with previous findings, where Canan *et al.* reported a PVA characteristic peak at $2\theta = 19.516^\circ$ [20]. Figure 4 shows the XRD patterns of pure and dye-doped PVA films. For the 3 wt% β -carotene-doped PVA film, a single peak at $2\theta = 19.60^\circ$ was observed, indicating that β -carotene was homogeneously dispersed within the PVA matrix and maintained the crystalline structure. Similarly, the 3 wt% lutein-doped PVA film exhibited a peak at $2\theta = 19.55^\circ$. While the addition of β -carotene increased the peak intensity, the incorporation of lutein did not significantly alter the peak intensity. These results suggest that both dyes are compatible with the PVA matrix without disrupting its crystalline structure.

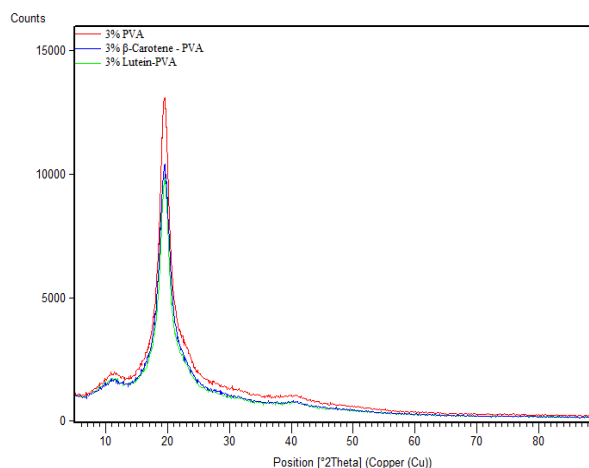


Figure 4. XRD graph of pure and dye-doped PVA films

The mechanical properties of the films were evaluated by tensile testing of pure and dye-doped PVA films. The 3 wt% pure PVA film exhibited a tensile strength of 37.97 MPa and a elasticity modulus of 158.8 MPa. For the 3 wt% β -carotene-doped PVA film, the tensile strength increased to 46.56 MPa, while the elasticity modulus decreased to 36.85 MPa, specifying that β -carotene incorporation enhanced the tensile strength but reduced stiffness. In contrast, the 3 wt% lutein-doped PVA film showed a tensile strength of 35.24 MPa and elasticity modulus of 91.61 MPa, suggesting a slight decrease in tensile strength upon lutein addition. The tensile properties of all samples are summarized in Table 1.

Table 1. Tensile strength and E modules of samples

Samples	E module (MPa)	Tensile strength (MPa)
3 wt % pure PVA film	158.89	37.97
3 wt % β -carotene-PVA film	36.85	46.56
3 wt % lutein-PVA film	91.61	35.24

Thermal characterization of the films was performed using differential scanning calorimetry (DSC) to determine their melting temperatures (T_m) and enthalpy values. The DSC curve of the 3 wt% pure PVA film is presented in Figure 5. The melting temperature of pure PVA was observed at 116.2 °C, with an enthalpy of -70.45 J/g, which is consistent with the reported T_m of ~200 °C for PVA [21]. For the 3 wt% β -carotene-doped PVA film, the melting temperature increased to 120.1 °C and the enthalpy to -104.4 J/g, as shown in Figure 6. Similarly, the 3 wt% lutein-doped PVA film exhibited a T_m of 126.5 °C and an enthalpy of -115.8 J/g (Figure 7).

The presence of endothermic peaks in all samples corresponds to phase transitions of the polymer matrix. These results indicate that the incorporation of β -carotene and lutein into PVA films increased the melting temperature, with lutein-doped films showing the highest T_m . Moreover, the enthalpy values increased upon dye addition, suggesting enhanced thermal stability of the dye-doped films compared to pure PVA.

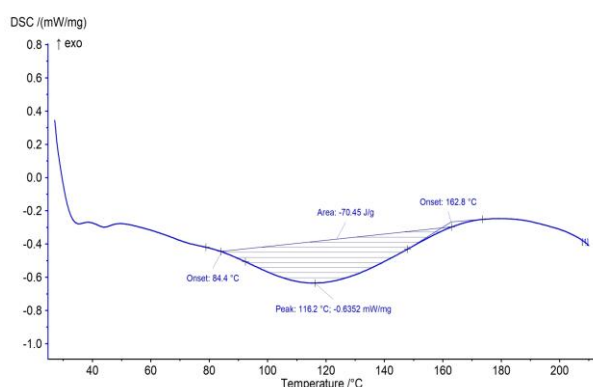


Figure 5. DSC graph of 3 wt % pure PVA film

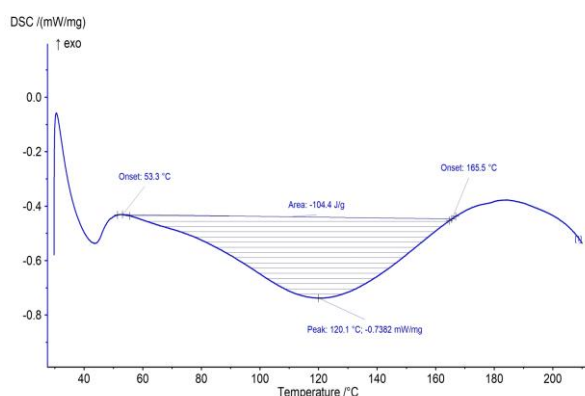


Figure 6. DSC graph of 3 wt % β -carotene dye-doped PVA film

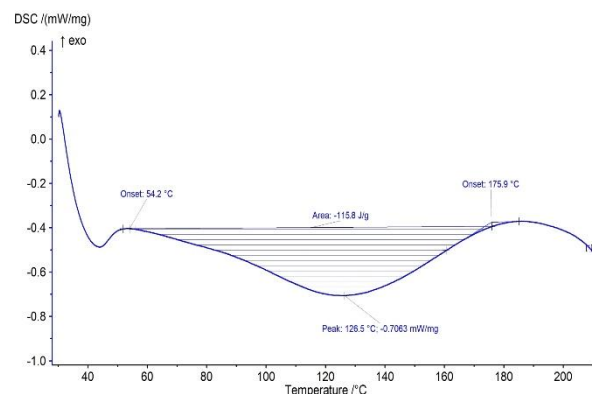


Figure 7. DSC graph of 3 wt % lutein dye-doped PVA film

CONCLUSION

In today's industry, dye-doped polymer-based films are frequently used in various areas. According to the findings of this study, the produced pure and dye-doped films exhibit favorable characteristics due to their crystal structure, smooth surface and good durability and have potential for packaging applications. Furthermore, these films have profits in terms of production conditions, usability, and biodegradability, supporting their potential use in multiple industrial areas. Considering the limitations of the solution casting method for large-scale production, alternative fabrication techniques could be explored to develop films at higher volumes. Additionally, these films may be combined as composite materials in lamination processes for various applications across different industries.

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Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation: During the preparation of this work the authors used ChatGPT to improve readability and language. The analysis data was visualized by generating Python code using Google Colab support.

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