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TiO_2 incorporated into a blend of biopolymeric matrices improves film properties and affects the postharvest conservation of papaya fruits under UV light

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ABSTRACT

This work investigated the properties of chitosan-cassava starch biopolymeric films containing nanometric photoactive TiO_2 particles for use in postharvest conservation of papaya fruits under UV light at a temperature of 15±1℃ and a relative humidity of 90±1% for 24 days. Starch-chitosan blend films showed intermediate hydrophobicity and improved mechanical properties. The addition of 1% TiO_2 into the polymeric matrix of starch/chitosan (1:1) further improved the mechanical properties with solubility of 16.04 ± 0.41%, visible transmittance of 31.76 ± 1.58%, and reduced UV transmittance of more than 97%. However, the addition of TiO_2 exceeding 1% led to the formation of agglomerates and excessive reduction in film transparency. UV exposure damaged the fruit peel and resulted in a higher weight loss. In contrast, the addition of 1% TiO_2 to the blend reduced the weight loss in light and dark by 7.12 ± 1.57% and 5.27 ± 0.31% respectively, and delayed fruit ripening.

Keywords: Chitosan/cassava starch nanocomposites, TiO_2 nanoparticles, *Carica papaya* L., UV absorbing coatings, edible fruit coatings, postharvest quality preservation.

1. Introduction

Papaya fruits (*Carica papaya* L.) are considered a good source of vitamins A and C, calcium, iron, potassium, magnesium, and sodium, besides phenolic, carotenoid, flavonoid, or amino acid compounds, and exhibit free radicals scavenging capabilities (Parven et al., 2020). Papayas also exhibit intense metabolic activity and high perishability as they present climacteric behavior with high ethylene production and respiration rates (Batista et al., 2020; Mendy et al., 2019). Conventional methods to maintain the postharvest quality of papayas in storage include physical (high and low temperature) and chemical (fungicide, oil, wax and others) treatment (Rodrigues et al., 2021). However, the use of cold storage, at approximately 10 °C, is more desirable due to the low risk of physiological damage to the fruits and the use of preservatives such as pesticides and fungicides need to be avoided due their toxicity, since there are promising alternatives that can replace them (Rodrigues et al., 2021; Braga et al., 2020; Arezoo et al., 2020).

Innovative and inexpensive strategies have been explored (Gopi et al., 2019; Yang et al., 2022; Huang et al., 2023a) to prolong fruits' shelf-life and reduce postharvest waste (Huang et al., 2023b). Active and smart biodegradable packaging, either as edible coating or films, interacts with the fruit products and thereby decreasing their metabolism and consequently preserving sensory and nutritional properties for a longer period (Kaewklin et al., 2018; Xing et al., 2020). Additionally, both the high antifungal activity of polymers, such as chitosan and the insertion of nanoparticles in the filmogenic solution resulted in reduced water vapor permeability rate and microbiological growth (Paiva et al., 2020) and thus delaying senescence of fruits and vegetables.

Cassava starch and chitosan are polymers with high film-forming ability, providing important benefits when used alone and/or in blend compositions (Gopi et al., 2019; Lim et al., 2020; Santacruz et al., 2015). In general, blend films present improved properties due to interactions that may occur in the mixed matrix, such as those between the NH_3^+ group from protonated chitosan and the hydroxyl groups of the starch (Cazón & Vázquez, 2020; Santacruz et al., 2015). However, films based on biopolymers may display a great affinity with water in addition to poor mechanical characteristics. In this context, the addition of nanoparticles into the biopolymer matrix has benefited edible coatings properties (Alizadeh-Sani et al., 2020; Arezoo et al., 2020; Fonseca et al., 2020; Paiva et al., 2020; Qu et al., 2019; Siripatrawan & Kaewklin, 2018). In general, papayas show a good appearance when preserved unpackaged at 12 ºC for up to 20 days of storage (Braga et al., 2020). On the other hand, if papaya is maintained at higher temperatures (25 ± 2 ° C), its shelf life is significantly reduced to seven days.

Film properties, such as water vapor barrier, solubility, mechanical, and optical characteristics, are important parameters in packaging procedure. The incorporation of nano-TiO_2, which have suitable dispersion, biocompatibility, and non-toxic characteristics, improves the hydrophobicity and mechanical properties of the biopolymer matrix (Alizadeh-Sani et al., 2020; Arezoo et al., 2020; Fonseca et al., 2020; Menezes et al., 2021; Qu et al., 2019; Siripatrawan & Kaewklin, 2018). TiO_2-polymer nanocomposites are widely regarded as safe for use in food packaging films due to the very low migration of TiO_2 of less than 0.1μg/kg from the packaging materials to the food (Zhang & Rhim, 2022). While toxicity and particle migration need to be further investigated in future studies, TiO_2 is thus far recognised as a safer material in food and pharmaceutical industries (Siripatrawan & Kaewklin, 2018; Alizadeh-Sani et al., 2020; Arezoo et al., 2020).

Furthermore, TiO_2 absorbs ultraviolet (UV) light (Achachlouei & Zahedi, 2018; Arezoo et al., 2020; Fonseca et al., 2020; Sadeghi-Varkani et al., 2018) and produces reactive oxygen species (ROS) and hydroxyl radicals, which may inactivate microorganisms and deplete ethylene (Kaewklin et al., 2018; Qu et al., 2019; Siripatrawan & Kaewklin, 2018). ROS and hydroxyl radicals are strong oxidizing agents that oxidize ethylene to CO_2 and H_2O and thus delaying the fruit's senescence and keeping nutritional quality for a longer time. Such effects were observed in chitosan/nano-TiO_2 coated mangoes (Xing et al., 2020) and in chitosan/nano-TiO_2 coated tomatoes (Kaewklin et al., 2018. In principle, the incorporation of TiO_2 in biopolymeric food packaging may minimise the negative impact of UV exposure on papaya fruits and prolong the fruits' shelf life through beneficial generation of ROS and reduction of scald damage. Nevertheless, the effect of photoactive TiO_2 on the properties of biopolymeric blend of chitosan-cassava starch and its impact on the conservation of papaya during storage in presence of UV light is yet to be elucidated.

We report herein the development of chitosan/cassava starch/TiO_2 bio-nanocomposites as a promising solution to maintain the postharvest quality of papayas. While previous studies have shown promising postharvest conservation of papayas using either chitosan (Braga et al., 2020) or cassava starch-based coatings with essential oil (Batista et al., 2020), there is a knowledge gap on the use of the blends and the incorporation of nano-TiO_2 into the mix of natural polymers. We address this gap by systematically evaluating the influence of chitosan and nano-TiO_2 contents on the water vapor permeability, solubility, mechanical, and optical properties of cassava starch-based bio-nanocomposites for use as coatings for papayas (*Carica papaya* L.) under both the absence and presence of UV light. The novel findings presented herein should provide a basis for further development of bio-nanocomposites with photoactive components, such as TiO_2, to maintain the postharvest quality of highly perishable fruits and reduce unnecessary postharvest waste.

2. Materials and methods

2.1. Synthesis of films

Commercial chitosan with 85% deacetylation was purchased from Polymar Indústria e Com. Imp. and Exp. Ltda – Brazil; while cassava starch was supplied by Indústria Primícia do Brasil Ltda - Brazil. Anatase titanium dioxide (TiO_2) with particle diameters of 20 - 25 nm and purity of 99.7% was obtained from Sigma-Aldrich, and the glycerol 99.5% purity was acquired from Dinâmica Química Contemporânea Ltda - Brazil. Chitosan films were prepared based on the method described by Rambabu et al. (2019). Cassava starch films were developed according to Oliveira et al. (2018) previous report. Biopolymers blend films (Chitosan/Starch-Cassava) and films containing nano-TiO_2 were prepared based on the method described by Menezes et al. (2021). The obtained films were conditioned at 23°C and 55% relative humidity (RH).

2.2. Design of experiment for films development

In this study, experiments were carried out using a full factorial design approach with a central point and axial points were added to fit in a quadratic model when the response variables were not adequately described throughout a linear empirical model. Two independent variables were then used (K=2 factors), denoted herein as X_1 = percentage of chitosan (CH) and X_2 = percentage of nano-TiO_2 with a range of, respectively, 0-100% and 0-2%, to study its effects on the properties of water vapor permeability (WVP), solubility (Sol), tensile strength (TS), elongation on rupture (ME), modulus of elasticity (EI) and opacity (Op) of cassava starch-based bio-nanocomposites. The percentage of glycerol was kept constant (20%) with regards to biopolymers' dry mass. The design of experiment coded and actual values for independent variables are shown in Table 1.

2.3. Films characterization

Assessments related to thickness and water vapor permeability of the films were performed as described by Monteiro et al. (2018). Morphology evaluations were carried out on the fractured surface and cross-section of the film via mechanical tests coupled with a scanning electron microscope (SEM) (Model VEGA 3, TESCAN). The samples were coated with a thin layer of gold by using a vacuum metallizer (model Q150R) for 5 min at 20 mA. The film surface was imaged with an acceleration voltage of 10 kV and a magnification of 5 kx; while the cross-section was imaged with an acceleration voltage of 5 kV and a magnification of 500x. Working distances were about 15 mm for all micrographs.

The mechanical properties were performed according to ASTM D882-83 standard applied to the Testing Machine DL5000/10000, Series EMIC 23, at speed of 5 mm/min with the application of a total force of 5 KN. The percentage of solubility was measured using methods described by Oliveira et al. (2018).

Film absorbance and transmittance were assessed with a UV-vis spectrophotometer, (THERMO model EVO-600PC). Opacity (AU.Nm / mm) was calculated by dividing the absorbance at 600 nm by film thickness [in millimeters] (Achachlouei & Zahedi, 2018). The water vapor permeability (g.mm/kPa.m^2.h) was calculated based on the weight (W) of water that permeates through a film of certain average thickness (L) and exposed area (A) within a given timeframe (t) and a water vapor pressure differential (ΔP). The water vapor permeability was calculated as follows: Equation (1):

$$\mathrm{WVP} = {W.L}/{A.t.\Delta P} \quad (1)$$

Film colour parameters, L (brightness), a (green and red), and b (blue and yellow), were estimated by reflectometry coupled with a portable colorimeter (Konica Minolta Sensing Inc. Japan) referenced by a standard black background ($L^* = 1$, $a^* = 0$ and $b^* = 0$). The total color difference (*ΔE*), whiteness (*WI*), and yellow (*YI*) indices of the samples were calculated using Eqs. (2)-(4), respectively, as described by Sadeghi-Varkani et al. (2018).

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \quad (2)$$

$$WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \quad (3)$$

$$YI = 142.86b/L \quad (4)$$

2.4. Application of edible coatings on papaya fruits and experimental setup

Papaya fruits (*Carica papaya* L.) were purchased from producers located in Mossoró, state of Rio Grande do Norte, Brazil, at commercial maturity (indicated by 15% of yellow streaks), free of damages, and in standardized sizes. All fruits were immersed in a sterilizing solution (100 mg/L sodium hypochlorite for 10 min.) and dried under natural conditions on a bench. Three types of treatment were devised – T1: uncoated papaya (control), T2: coated papaya fruits containing chitosan/cassava starch edible coating (1:1), and T3: coated papaya fruits containing chitosan/cassava starch (1:1) with 1% TiO_2. Except for the control fruits T1, all fruits in T2 and T3 were immersed in a specific filmogenic solution (with or without TiO_2 1%) for 90 s and then removed and dried at a temperature of 23ºC for 1.0 h. In alignment with the recommended optimum conditions for commercial storage (Rodrigues et al., 2021), fruits of each treatment were then conditioned in different cold chambers at 15 ± 1 ºC and 90 ± 1% RH for 24 days. In one of the chambers, the samples were subjected to ultraviolet (UV) light irradiation from a 9 W lamp of 25 mm x 120 mm (model CUH9L, GRECH) with wavelength range of 230 – 430 nm. In such conditions, coated and uncoated fruits were placed at 15 cm from the lamp and exposed to UV light for 2 min on the first day and subsequently every seven days, with a total exposure of 8 min that is equivalent to 1.68 kJ m^{-2} throughout 24 days of storage.

2.5. Quality of papaya fruits evaluations

Weight loss of the papaya fruits was estimated by the percentage difference between the initial and final weight over the storage time. Fruit firmness, expressed in Newton, was evaluated by dividing the fruit into two parts and, in one of them, five readings were carried out on the pulp at random and equidistant locations using a Penetrometer (model FT 327, McCormick, USA) with a tip diameter of 8 mm. Soluble solids content (SS) was expressed in °Brix (digital refractometer model PR - 100 Palett, Atago, Japan), while titratable acidity (TA) was expressed in g of citric acid per 100 g of fruit juice. pH (digital potentiometer) was measured with a method previously described by Paiva et al. (2020). Fruit vitamin C content was expressed in mg of vitamin C per 100 g pulp, as reported by Oliveira et al. (2018).

The peel colour was determined by reflectometry, using a CR-10 colorimeter (Konica Minolta®, Japan). The readings were expressed in brightness (*L*), chromaticity (*C*) and angle Hue (*H*). The measurements were averaged from three equidistant points. External (*AE*) and internal (*AI*) appearances were evaluated by a visually subjective rate scale with grades ranging from 5 to 0 according to the severity of imperfections on external (depression, wilting, fungal lesions, or stains) and internal (internal collapse, aberrant seeds and/or the presence of liquids in the seed cavity) areas. Thus, the lower the *AE* and *AI* scores, the lower was the fruit overall quality. Fruits with a score below 3.0 were considered unsuitable for commercialization (Paiva et al., 2020).

2.6. Statistical analysis

The response behavior of the films was analyzed by an empirical polynomial model. The models were verified to be statistically significant at $P<0.05$ with an analysis of variance (ANOVA) and F test. The significant models were presented in response surface graphs. For the quality analysis of the fruits, a factorial design (2×3) was used by considering two conditions, i.e. presence and absence of UV light, and three treatments, i.e. T1, T2, T3, with four replicates. A two-way ANOVA and Tukey test were used, being considered significantly different at $P<0.05$. All statistical analysis of the data was carried out by design of experiment with Statistica® software version 13.5 (TIBCO Software Inc., USA).

3. Results

3.1. Physicomechanical properties

The parameters used in the design of experiment with both coded and actual values for independent variables as well as the values obtained for the studied response variables at each point are shown in Table 1. Films absent of chitosan (starch films) plus TiO_2 showed lower WVP as compared to its counterparts, thereby presenting a value of 7.78 g.mm/kPa.m^2.h in starch films containing 2 % TiO_2 (run 3). As for solubility, starch films with or without TiO_2 were more soluble (runs 3 and 1, respectively) than chitosan films with or without TiO_2 (runs 4 and 2, respectively). For solubility, there is a strong influence of chitosan and TiO_2, in which the lowest value was exhibited by the biopolymer blend containing nano-TiO_2.

Greater tensile strength are observed in chitosan films as compared to starch films. The addition of 1% TiO_2 resulted in films with higher tensile strength. However, a higher concentration of TiO_2 leads to more brittle films. The highest tensile strengths were found in run 6, which corresponds to chitosan films with 1% TiO_2, and in run 11, which is the 1:1 blend of biopolymers containing 1% TiO_2, with values of 59.46 MPa and 54.53 MPa, respectively. In terms of elongation at break, cassava starch films (run 1) showed a higher elongation than chitosan films (run 2). When these two biopolymers are mixed in a 1:1 ratio, there is an increase in elongation (run 5), which becomes more substantial with the addition of 1% TiO_2 to the blend (run 10). The elongations of the starch (run 1), blend only (run 5), and blend with 1% TiO_2 films (run 10) were found at 8.32%, 11.06% and 25.96% respectively, coupled with a reduction in the modulus of elasticity.

The opacity of the films was observed to increase in response to the addition of TiO_2, while decrease with the addition of chitosan. The opacity shows a lower value of 0.79 AU.Nm/mm in chitosan films (run 2) and a higher value of 22.98 AU.Nm/mm in starch films containing higher TiO_2 concentration (run 3). Blending with 1% TiO_2 shows intermediate values of around 9.92 AU.Nm/mm (Table 1).

Table 2 shows the coded models to describe water vapor permeability (Y_1), solubility (Y_2), tensile strength (Y_3), elongation at break (Y_4), modulus of elasticity (Y_5), and opacity (Y_6) of the studied bio-nanocomposites within the experimental domain along with the fitting values of R^2, $R_{adjusted}$, $F_{calculated}$ and $F_{critical}$ for the models. The omitted coefficients are not significant, thus being disregarded in the adjusted models. The R^2 values are all higher than 0.85, except for the coded model for elongation at break with an R^2 of 0.69. In addition, $F_{calculated}$ are all higher than $F_{critical}$ for a 95% confidence level, indicating that the models are statistically significant.

Fig. 1 shows the response surfaces to demonstrate the effect of chitosan and nano-TiO_2 contents on WVP (a), solubility (b), tensile strength (c), elongation at break (d), modulus of elasticity (e), and opacity (f) of the cassava starch/chitosan/TiO_2 nanocomposite films. Fig. 1a shows WVP as a function of the percentages of chitosan and nano-TiO_2, where WVP increases with the increase of TiO_2 concentration, which was markedly evidenced by the presence of chitosan. Intermediate values are observed with the blend formation and a slight reduction in starch films. Fig. 1b shows the variation of solubility, where the most soluble films contain only cassava starch. Chitosan and TiO_2 have a strong influence on solubility, where films with 67.5% chitosan and 1.2% TiO_2 expected to exhibit the lowest solubility. Fig. 1c shows the variation in tensile strength, where starch films without the addition of chitosan show lower tensile strength but increasing with the addition of chitosan. Excess chitosan does not affect tensile strength. However, there are reductions when the added TiO_2 have concentrations higher than 1%. This reduction is more pronounced in cassava starch films (0% chitosan). The highest tensile strength can be potentially achieved by 100% chitosan and 0.8% TiO_2. Fig. 1d shows the values of elongation at break, where films without TiO_2 were exhibited higher elongation in the 1:1 mixture of polymers. With the incorporation of TiO_2, the highest elongation can be potentially achieved by the addition of 50.6% chitosan and 0.8% TiO_2. Fig. 1e shows that the modulus of elasticity has an opposite behavior to the elongation. There is a minimum point observed at a composition of 40.9% chitosan and 0.8% TiO_2, suggesting that films with this composition are less rigid and, consequently, more flexible (Fig. 1d). Fig. 1f shows the opacity that increases with a decrease in chitosan concentration and an increase in TiO_2 levels.

3.2. Morphological analysis

Fig. 2 shows surface and cross-sectional SEM images of pure chitosan, pure cassava starch, and chitosan/cassava starch biofilms. Fig. 2a-c were taken from pure chitosan biofilms CH, CH/T 1%, and CH/T 2 % respectively, Fig. 2d-f were taken from pure cassava starch ST, ST/T 1%, and ST/T 2% respectively, and Fig. 2g-i were taken from chitosan/cassava starch (1:1) CH/ST, CH/ST/T 1%, and CH/ST/T 2% respectively.

Pure chitosan films (CH) exhibit homogeneous surface appearance with marks of moderately ductile fracture (Fig. 2a). In contrast, pure casava starch films (ST) show highly heterogeneous surface appearance with marks of brittle fracture (Fig. 2d). A blend of chitosan and cassava starch (CH/ST) recovers the surface homogeneity and apparent ductile fracture behaviour (Fig. 2g). The addition of TiO_2 further increases the heterogeneity of the biofilms. The addition of TiO_2 further increases the heterogeneity of the biofilms. Agglomerated TiO_2 and empty spots can be observed in the cross-sectionon chitosan/cassava starch (1:1) films with 2% w/w TiO_2 (CH/ST/T 2%) (fig. 2i) and in chitosan films with TiO_2 (CH/T1%, CH/T2%) (Fig. 2b, c) respectively. In addition, all cassava starch films (ST) TiO_2 enhanced exhibit marks of brittle fracture (Fig. 2e, f).

Fig. 3a shows the UV-vis absorbance spectra of the films. The chitosan/cassava starch blend showed a peak absorbance at 221 nm. The addition of 1% TiO_2 resulted in a higher absorbance in the visible and UV wavelengths with a peak in the range from 240 nm to 360 nm. The addition of 1% TiO_2 to the chitosan/cassava starch blend (CH/ST/T 1%) led to a significant reduction ($p \leq 0.05$) in transmittance of up to 97% in the UV region and 60% in the visible region than the TiO_2-absent CH/ST films (Table 3). Note that the addition of 1% TiO_2 did not significantly alter the average thickness of the biopolymer blend films, which was 0.06 ± 0.01 mm for CH/ST. Table 3 also shows the luminosity (*L*), total colour difference indices (*ΔE*), whiteness indices (*WI*), yellow indices (*YI*) of CH/ST and CH/ST/T 1%. All colour parameters were found to be dependent on TiO_2 concentrations. The addition of 1% TiO_2 led to significant increases in *L*, *ΔE*, and *WI*. In contrast, the yellow index (*YI*) decreases with the addition of TiO_2.

3.3. Effects of coating on the quality of papaya fruit in the absence and presence of UV light

Table 3 presents the evolution of physicochemical properties of papaya fruit within 24 days of storage while being coated with CH/ST and CH/ST/T 1% films in the presence and absence of UV light exposure at a constant temperature and humidity of 15 ± 1 ºC and 90 ± 1% RH, respectively. Although UV light has not been implemented in industrial practice for postharvest treatment, these temperature and humidity conditions are well aligned within the recommended optimum conditions for commercial storage of papaya fruits (Rodrigues et al., 2021). The effect of edible coatings (CH/ST and CH/ST/T 1%) on the weight loss of papaya fruit is insignificant compared to the control papaya fruit without coatings. The fruits with TiO_2 containing coatings (CH/ST/T 1%) exhibit significantly lower variation in light and dark weight losses the fruit showed a higher weight loss, except for those with coatings containing TiO_2 (Table 3). Both control and fruits without TiO_2 containing coatings (CH/ST) exhibit significantly higher weight loss in the presence of UV than those in the absence of UV light. The effect of UV light on pulp firmness was found to be negligible. Although the presence or absence of light does not affect the pulp firmness, it is worth noting that the coatings, both with and without TiO_2, led to a higher pulp firmness than the control. Pulp firmness increased from 1.58 ± 0.16 N for uncoated fruits to 4.77 ± 0.29 N and 5.65 ± 1.84 N for coated fruits with and without TiO_2, respectively. However, the presence of TiO_2 did not significantly affect between coatings.

The exposure to UV light was found to result in a significantly lower titratable acidity (TA) in all fruits. The exposure to UV light was also found to cause a slight reduction in the ascorbic acid (AA) content of the coated fruit, although it was not significant. Surprisingly, under dark conditions, the TiO_2 containing coatings (CH/ST/T 1%) led to a significant reduction in AA. Furthermore, the influence of UV light and coatings on soluble solids (SS) and pH was found to be negligible. SS and pH were measured to be relatively constant between 12.70 ± 0.25 and 13.60 ± 0.58 and between 5.41 ± 0.12 and 5.60 ± 0.04, respectively.

Table 3 shows the parameters of colour, luminosity (*L*), chroma (*C*), and hue angle (*H*) of the fruit peel. The exposure to UV light significantly modified *L* of the fruit peel. Under UV light, the coated fruits showed a significant reduction in *L* and *C* in contrast to the uncoated fruits. However, in dark conditions, there was no significant difference in *L* between coated and uncoated fruits. Nevertheless, the coated fruits had lower *C* than the uncoated ones. Regardless of light or dark condition, *H* of coated fruits is significantly higher than that of control. This indicates that coated fruits were able to maintain their green colour better than the uncoated ones with yellowish colour. Fig.3c shows the influence of coatings and UV light on the colour of the papaya fruit peel. *H* of the coated fruits was influenced by the UV light exposure. The presence of TiO_2 in the coating resulted in H of 102.37 ± 1.97 in light conditions, which was significantly higher than that in the dark condition with H of 93.91 ± 1.77.

Fig. 3b shows external and internal appearance of papaya fruit upon different coatings, both in the presence and absence of UV light. The coated fruits kept external appearance ratings above 3.8. All coatings were effective in maintaining the internal appearance score above 3.0, in both light and dark conditions. Moreover, fruits that were coated with TiO_2 containing films were scored an internal appearance of above 4.0. However, only the control fruit did not pass the acceptable internal appearance grade for commercialization of 3.0.

4. Discussion

As described above, there is a strong influence of polymers concentration in the blend and TiO_2 levels on WVP. The reduction of OH^- groups improves the WVP of the film (Cheng et al., 2022), in addition the blend of chitosan and starch may lead to interactions between NH_3^+ (protonated chitosan) and OH^- (starch) functional groups that provide suitable properties (Cazón & Vázquez, 2020; Santacruz et al., 2015). Likewise, the incorporation of nano-TiO_2 at an optimal concentration can prevent water vapor from diffusing through the film, as it is insoluble in water, increasing the diffusion pathway. It can also improve the interaction with the hydrophilic groups -OH and -NH_2, turning the film more hydrophobic (Al-Sagheer & Merchant, 2011; Sadeghi-Varkani et al., 2018). These findings are in agreement with previous studies, where a reduction in WVP of sago starch films can be introduced by an increase in TiO_2 concentration (Arezoo et al., 2020) and the addition of 1% TiO_2 into gelatin films led to a reduction in water-polymer interactions while that of 2% TiO_2 led to an increase in WVP due to the formation of larger TiO_2 agglomerates (Fonseca et al., 2020). This suggests that nano-TiO_2 interact with the biopolymer groups by hydrogen bonds and thus weakening the interactions between polymer and water molecules (Alizadeh-Sani et al., 2020; Arezoo et al., 2020; Fonseca et al., 2020; Sadeghi-Varkani et al., 2018; Siripatrawan & Kaewklin, 2018).

For the tensile strength, the added nano-TiO_2 with concentrations higher than 1% are likely to result in agglomerations that act as stress concentration sites and thus making the film brittle. A suitable dispersion of nano-TiO_2 is, however, non-trivial to achieve, as it is dependent on the surface interaction between the nanoparticle and the biopolymer matrix. For instance, the incorporation of 1% of TiO_2 causes agglomeration of nanoparticles in hydroxypropylmethylcellulose (HPMC-TiO_2) nanocomposites while such agglomeration does not occur in gelatin-TiO_2 nanocomposites (Fonseca et al., 2020). While the increase in TiO_2 content leads to more brittle films, it provides an effective means to modify the mechanical properties of the films (Alizadeh-Sani et al., 2020; Qu et al., 2019). As described above, the increase in nano-TiO_2 leads to a higher elasticity modulus in films with lower chitosan contents. However, without TiO_2, films with higher contents of chitosan are more rigid. Chitosan (CH) films have a more uniform surface with denser exfoliations in the mechanical rupture section, which indicates less ductile fracture (Fig 1). The addition of TiO_2 in chitosan film favours agglomerations of nanoparticles and the appearance of voids in the fracture section. This is more pronounced with an increase in TiO_2 to 2% (Fig. 2b, c), which also leads to higher WVP values (Fig. 1a) and higher solubility (Fig. 1b). In contrast, starch films (ST) have a rougher surface and fracture section with cracks that indicate brittle fractures (Fig. 2d). The amylose and amylopectin present in the starch provide greater mobility and brittleness due to the mixture of these polymers, in addition to the higher number of hydrophilic groups that can interact with water. It is also observed that the addition of TiO_2 reduces the solubility. Furthermore, the addition of higher levels of TiO_2 leads to agglomerations of nanoparticles that act as stress concentration sites and results in brittle films as shown by the fracture section in response to the addition of 1 and 2% of TiO_2 (Fig. 2e, f). In this study, films with higher starch contents are found to be the most soluble and brittle (Fig. 1b, c, d).

Biopolymeric films with mixture of chitosan and cassava starch (CH/ST) show intermediate characteristics in both the surface and fracture sections and exhibit a crack reduction that indicates a more ductile fracture (Fig. 2g). Also, previous studies based on the use of different types of gelatin showed improved mechanical characteristics (Ashrafi et al., 2023). Notably, the addition of 1% TiO_2 into the blend (CH/ST/T) affects the surface roughness of the films as indicated by the appearance of small TiO_2 agglomerations. This is in agreement with previous study where the addition of TiO_2 leads to the apparent increase in surface roughness of hydroxypropylmethylcellulose (HPMC-TiO_2) and gelatin (gelatin-TiO_2) films (Fonseca et al., 2020). Altogether, these CH/ST/T films show a more compact matrix in the fracture section (Fig. 2h) with suitable mechanical properties of intermediate WVP value and low solubility. In this study, CH/ST/T films containing 40.8–67.5% of CH and 0.8–1.2% nano-TiO_2 exhibit the optimal mechanical properties, solubility, and suitable transparency along with acceptable intermediate WVP values. This finding motivates us to select two formulations for use as a coating to maintain the postharvest quality of papaya in the presence of UV light, i.e., CH/ST blend (1:1) - with and without 1% nano-TiO_2.

It is important to note that an increase in TiO_2 levels leads to a significant increase in *L*, *ΔE,* and *WI* due to the inherent white colour of nano-TiO_2. The yellow index (YI) was higher in the blend without TiO_2, where the chitosan and cassava starch films exhibit a YI of 49.72 ± 0.21 and 47.36 ± 0.23, respectively. The addition of TiO_2 significantly reduce YI in the blend due to the white colour of the nanoparticle. A similar behaviour is also reported in previous study when 1% TiO_2 was added into the polymer hydroxypropylmethylcellulose (HPMC-TiO_2) and gelatin (gelatin-TiO_2) matrices (Fonseca et al., 2020). The addition of 1% TiO_2 to the CH/ST blend films with suitable optical properties can provide excellent prevention against damage induced by ultraviolet light to the fruit. This is in agreement with previous study where TiO_2 delays the ripening of tomatoes due to the photocatalytic degradation of ethylene in the atmosphere (Kaewklin et al., 2018; Maneerat & Hayata, 2008). In addition, it reduces the respiratory peak of mangoes in an ethylene-enriched atmosphere with ultraviolet light as a source of irradiation (Chiara et al., 2015), which ultimately preserves their sensory and nutritional properties for a longer period (Xing et al., 2020).

The measured weight loss (WL) is mainly related to water loss by transpiration of fruit. It is thus necessary to minimise WL to maintain the product quality during storage (Batista et al., 2020). Despite the strong influence of chitosan and TiO_2 contents in decreasing the solubility of the films (Fig. 1b), such coatings (CH/ST and CH/ST/T1%) does not demonstrate the lowest WVP values (Fig. 1a). The higher WL under light suggests the occurrence of damage to the fruit. Note that an ideal level of UV light is an important factor in preventing this fruit. Previous studies suggest that the application of lower than 3 kJ m^{-2} of UV-C irradiation contributes to the effective management of postharvest mango diseases (Terao et al., 2015), while 39.6 kJ m^{-2} of UV-C radiation leads to an increase in postharvest losses of pineapple fruit (Sari et al., 2016). Similarly, the deleterious effects of UV-C irradiation on *Colletotrichum Gloeosporioides*, which the causal agent of anthracnose in papaya, may lead to a reduction in papaya losses during storage (Cia et al., 2007). The presence of 1.0% of TiO_2 in the CH/ST blend reduces the damage in fruits, since nano-TiO_2 absorb UV light, preserve cell membrane, and reduce the weight loss. Moreover, the presence of TiO_2 in the film reduces its transmittance (Table 3) and promotes ethylene degradation in the presence of UV light via the generation of hydroxyl radicals (•OH) and reactive oxygen species (ROS) (Siripatrawan & Kaewklin, 2018).

Regarding the pulp firmness, the coated papaya fruits are observed to delay their ripening during the shelf-life. The decrease in pulp firmness is due to chemical and biochemical reactions during its maturation, in which there is synthesis and activation of hydrolytic enzymes that act in the depolymerization of pectic substances of the cell wall (Ali et al., 2011). Previous studies using chitosan/TiO_2-coated mango fruits show a delay in respiratory peak, which maintains pulp firmness and nutritional quality by more than five days as compared to control at 13°C (Xing et al., 2020). Keeping pulp firmness is an important feature in the postharvest of fruits and it is intrinsically related to fruit quality during handling and transport (Mendy et al., 2019).

The lower titratable acidity values of the fruits under light suggest the occurrence of abiotic stress. This is more pronounced in uncoated fruits as their skin surfaces are exposed to a higher dosage of UV light. Furthermore, previous studies have shown that coatings provide a barrier to modify the internal atmosphere of the fruit and delay the degradation of organic acids, which is associated with fruit ripening delaying (Ali et al., 2011). Furthermore, the reduction in acidity is associated with metabolic changes in fruits since it is used as a substrate in the respiration process (Mendy et al., 2019). Ascorbic acid is known to increase during the ripening of papaya fruits (Ali et al., 2011). In this study, the reduction is acidity suggests a delay in the ripening of the fruits upon application of the coatings. This can also be observed by the fruits' ability to maintain their peel green colour (Fig. 3c) and ascorbic acid (AA) by the UV light, which are important indicators of healthy fruits (Hernández-Muñoz et al., 2006). Note that appearance is a determining factor in the acceptance of fruits by consumers and the change in skin colour from green to yellow is one of the most easily recognisable changes that occur during papaya maturation. The application of CH/ST films also allow the SS contents to remain suitable for commercialization. In agreement with previous study, chitosan coatings do not affect the SS content during papaya storage (Bautista-Baños et al., 2003).

Fruits with less light exposure than the control show lower chlorophyll degradation in the epidermal tissue of the fruit. Thus, lower lightness values of coated fruits under UV exposure may indicate a metabolic delay, which can be associated with a lower respiration rate and probably a reduction in ethylene evolution (Ali et al., 2011). The lowest chroma values detected in coated fruits suggest lower degradation of chlorophyll and synthesis of carotenoids in the papaya peel. In contrast, uncoated fruits show a strong yellow and orange pigmentation in 24 days (Fig. 3c). The hue angle of the skin of coated papaya fruit with the presence of TiO_2 in the presence of UV is significantly higher than that in dark conditions, which visually appear as greener colour fruits under light conditions. This suggests a photodegradation of ethylene when exposed to UV light, thereby delaying the ripening of papaya fruits, which is in agreement to previous study (Lourenço et al., 2017). As described above, the appearance of the yellow colour of the skin is due to the degradation of the chlorophyll molecule, which involves, among others, the activity of chlorophyllase enzyme and carotenoids biosynthesis (Jing et al., 2015). Previous studies on tomatoes have demonstrated that TiO_2 packaging delays ripening processes under UV exposure due to photocatalytic degradation of ethylene (Chiara et al., 2015; Kaewklin et al., 2018; Maneerat & Hayata, 2008).

Regardless of the treatment, we consider the external appearance to remain marketable after 24 days of storage. Under light conditions, the internal appearance of coated fruits containing TiO_2 (CH/ST/T1%) show absence or traces of defects below 10% (internal collapse, aberrant seeds, and presence of liquids in the seed cavity). In contrast, the control fruits exhibit advanced stage of senescence. Thus, this study demonstrates the promising potential for the use of photoactive edible coatings in maintaining the quality of papaya fruits in commercially relevant storage conditions. Under the presence of light, coatings with TiO_2 delayed the metabolism of the fruit with higher effectiveness than on uncoated and non-TiO_2 coated fruits. As UV irradiation may become a practical part of postharvest treatment, the use of bio-nanocomposites with photoactive components, such as TiO_2, may create a synergistic effect to maintain the postharvest quality of highly perishable fruits. These findings lay the foundation for further development and commercial viability study of active and sustainable packaging using biopolymers with added photoactive functionality, which is imperative for enabling a pathway to reduce unnecessary postharvest waste.

5. Conclusion

Cassava starch films containing chitosan and TiO_2 were developed, and the blend of cassava starch/chitosan (1:1) with the addition of 1% TiO_2 showed improved mechanical and physical barrier features. Moreover, there was a reduction in the film transmittance properties, which were higher than 97% in the UVA, UVB, UVC region as compared to the blend without TiO_2. UV light caused abiotic stress evidenced by an increased weight loss of the fruits. However, the coating containing 1% nano-TiO_2 into the matrix chitosan/starch (1:1) biopolymer blend promoted stress alleviation, characterized by fruit weight loss reduction and ripening delay, which was associated with the maintenance of green colour, pulp firmness, soluble solids, pH, and vitamin C for a longer period. Therefore, fruits coated by this renewable and biodegradable packaging kept their external and internal appearance with a suitable market quality for up to 24 days of storage under 15 ºC and 90 ± 1% RH conditions.

CRediT authorship contribution statement

Francisco Leonardo Gomes de Menezes: Conceptualisation, Methodology, Investigation, Formal analysis, Writing -original draft. **Edna Maria Mendes Aroucha:** Conceptualisation, Supervision, Writing - review & editing. **Adrianus Indrat Aria:** Conceptualisation, Writing - review & editing. **Francisco Klebson Gomes dos Santos:** Conceptualisation, Supervision, Writing - review & editing. **Ricardo Henrique de Lima Leite:** Conceptualisation, Writing - review & editing.

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.

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FIGURE LEGENDS

Fig. 1. Variation of WVP (a), Solubility (b) Tensile strength (c), Elongation at break (d), Modulus of elasticity (e) and Opacity (f) of cassava starch nanocomposite films, as a function of chitosan and nano-TiO_2 percentages.

Fig. 2. Scanning electron microscopy of the surface and cross section (inserts) of biofilms (a) CH, (b) CH/T 1%, (c) CH/T 2%, (d) ST, (e) ST/T 1 %), (f) ST/T 2%), (g) CH/ST, (h) CH/ST/T 1%) and (i) CH/ST/T 2%).

Fig. 3. UV-vis absorbance spectra of the films used as coatings (a), External and internal appearance of papaya fruit upon different coatings (b) and Illustration of papaya peel color (external appearance) and internal appearance upon different coatings (c), both in the presence and absence of UV light at 15±1ºC and 90±1% RH for 24 days of storage. Results are expressed as mean ± standard deviation (n = 3). Different lower-case letters indicate the statistically significant difference among treatments at the same light condition by Tukey's test ($P \leq 0.05$). Different upper-case letters indicate the statistically significant difference among light condition at the same treatment by Tukey's test ($P \leq 0.05$).

TABLE LEGENDS

Table 1 Experimental matrix presenting coded and real values for independent variables and mean values based on response variables. Y1 - Water vapor permeability (g.mm/kPa.m2.h), Y2

- Solubility (%), Y3 - Tensile strength (Mpa), Y4 - Elongation on rupture (%), Y5 - Modulus of elasticity (Mpa), Y6 -Opacity (AU.Nm/mm), (*) factorial design with center point.

Table 2 Proposed coded models to describe Y_1 - Water vapor permeability, Y_2 - Solubility, Y_3 - Tensile strength, Y_4 -Elongation at break, Y_5 - Modulus of elasticity, Y_6 - Opacity of the studied bio-nanocomposites within the experimental domain. (*) Statistically significant for $P<0.05$.

Table 3 Results of physical-chemical parameters of papaya fruit upon different coatings, both in the presence and absence of UV light at 15 ± 1 ºC and 90 ± 1% RH after 24 days of storage and parameters of the films used as coatings. Results are expressed as mean ± standard deviation (n = 3). Control: fruit without coating. Mean values on the same line with different lowercase letters indicate statistical difference ($P \leq 0.05$) based on Tukey's test. Mean values in the same column with different capital letters indicate statistical difference ($P \leq 0.05$) based on Tukey's test. * Titratable acidity (g equivalent of citric acid per 100g of pulp). ** Ascorbic Acid (AA) (mg of AA/100 g Pulp). *** Soluble solids (%).

Table 1 Experimental matrix presenting coded and real values for independent variables and mean values based on response variables. Y1 - Water vapor permeability (g.mm/kPa.m2.h), Y2 - Solubility (%), Y3 - Tensile strength (Mpa), Y4 - Elongation on rupture (%), Y5 - Modulus of elasticity (Mpa), Y6 -Opacity (AU.Nm/mm), (*) factorial design with center point.

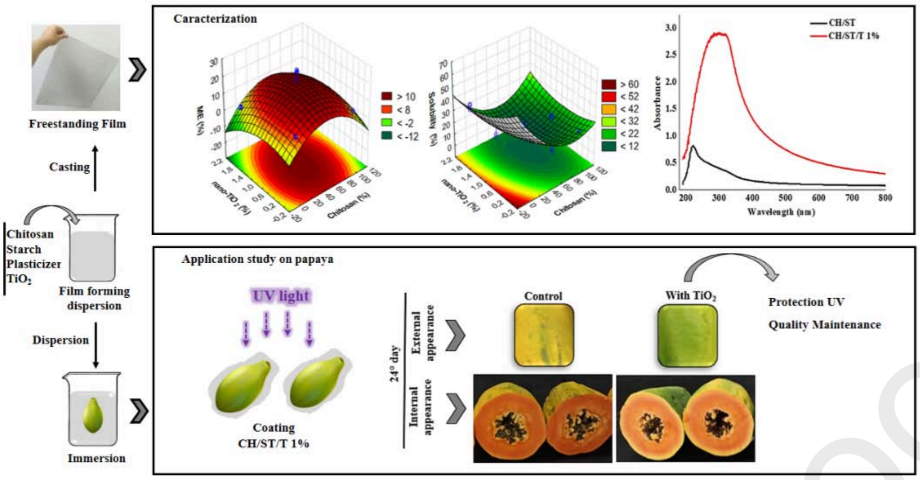
Run		Composition		Response variables					
		%CH (X_1)	%TiO_2 (X_2)	WVP* Y_1	Sol Y_2	TS Y_3	ME Y_4	EI Y_5	Op* Y_6
Factorial	1	0 (-1)	0.0 (-1)	9.55	49.71	29.30	8.32	867.33	13.51
	2	100 (+1)	0.0 (-1)	20.77	19.28	54.30	5.46	2534.27	0.79
	3	0 (-1)	2.0 (+1)	7.78	32.54	8.01	1.00	2962.98	22.98
	4	100 (+1)	2.0 (+1)	27.76	18.18	44.79	5.61	1726.48	9.01
Axial points	5	50(0)	0.0 (-1)	-	16.53	43.88	11.06	1236.01	-
	6	100(+1)	1.0 (0)	-	16.88	59.46	6.24	1552.32	-
	7	50(0)	2.0 (+1)	-	12.90	36.63	6.28	1064.34	-
	8	0(-1)	1.0 (0)	-	24.25	28.40	4.85	1047.01	-
Central points	9	50 (0)	1.0 (0)	14.84	16.04	49.76	24.61	440.44	9.97
	10	50 (0)	1.0 (0)	13.51	16.52	50.44	25.96	459.63	10.18
	11	50 (0)	1.0 (0)	16.10	16.10	54.53	25.01	469.00	9.34
	12	50 (0)	1.0 (0)	14.90	15.51	49.00	25.02	470.00	10.18

Table 2 Proposed coded models to describe Y_1 - Water vapor permeability, Y_2 - Solubility, Y_3 - Tensile strength, Y_4 -Elongation at break, Y_5 - Modulus of elasticity, Y_6 - Opacity of the studied bio-nanocomposites within the experimental domain. (*) Statistically significant for $P<0.05$.

Fitted models*	R^2	$R_{adjusted}$	$F_{calculated}$	$F_{critical}$
$Y_1 = 9.143 + 0.112 \cdot X_1 - 0.885 \cdot X_2 + 0.044 \cdot X_1 \cdot X_2$	0.970	0.962	127.69	3.49
$Y_2 = 44.952 - 0.702 \cdot X_1 + 0.004 \cdot X_1^2 - 18.374 \cdot X_2 + 5.352 \cdot X_2^2 + 0.080 \cdot X_1 \cdot X_2$	0.858	0.826	26.11	2.66
$Y_3 = 27.872 + 0.502 \cdot X_1 - 0.002 \cdot X_1^2 + 10.651 \cdot X_2 - 9.970 \cdot X_2^2 + 0.059 \cdot X_1 \cdot X_2$	0.967	0.963	229.62	2.42
$Y_4 = 6.711 + 0.323 \cdot X_1 - 0.003 \cdot X_1^2 + 7.360 \cdot X_2 - 5.609 \cdot X_2^2 + 0.037 \cdot X_1 \cdot X_2$	0.691	0.652	17.46	2.42
$Y_5 = 953.430 - 17.089 \cdot X_1 + 0.347 \cdot X_1^2 - 525.394 \cdot X_2 + 718.645 \cdot X_2^2 - 14.517 \cdot X_1 \cdot X_2$	0.943	0.935	128.58	2.42
$Y_6 = 13.186 - 0.127 \cdot X_1 + 4.738 \cdot X_2 - 0.006 \cdot X_1 \cdot X_2$	0.990	0.988	535.07	3.24

Table 3 Results of physical-chemical parameters of papaya fruit upon different coatings, both in the presence and absence of UV light at 15 ± 1 ºC and 90 ± 1% RH after 24 d of storage and parameters of the films used as coatings. Results are expressed as mean ± standard deviation (n = 3). Control: fruit without coating. Mean values on the same line with different lowercase letters indicate statistical difference (P ≤ 0.05) based on Tukey's test. Mean values in the same column with different capital letters indicate statistical difference (P ≤ 0.05) based on Tukey's test. * Titratable acidity (g equivalent of citric acid per 100g of pulp). ** Ascorbic Acid (AA) (mg of AA/100 g Pulp). *** Soluble solids (%).

Parameter		Formulations		
			Coating	
Papaya		Control	Without TiO_2 (CH/ST)	With TiO_2 (CH/ST/T 1%)
Weight loss (%)	Light	8.49 ± 0.67 ^{aB}	7.43 ± 1.14 ^{aB}	7.12 ± 1.57 ^{aA}
	Dark	5.80 ± 0.40 ^{aA}	4.63 ± 0.38 ^{aA}	5.27 ± 0.31 ^{aA}
Firmness (N)	Light	2.33 ± 0.27 ^{aA}	3.75 ± 1.37 ^{aA}	3.61 ± 1.19 ^{aA}
	Dark	1.58 ± 0.16 ^{aA}	5.65 ± 1.84 ^{bA}	4.77 ± 0.29 ^{bA}
TA*	Light	0.06 ± 0.00 ^{aA}	0.08 ± 0.00 ^{bA}	0.08 ± 0.01 ^{bA}
	Dark	0.10 ± 0.01 ^{aB}	0.10 ± 0.00 ^{aB}	0.10 ± 0.01 ^{aB}
AA**	Light	22.93 ± 3.26 ^{aA}	21.87 ± 0.92 ^{aA}	22.53 ± 2.41 ^{aA}
	Dark	28.27 ± 1.01 ^{aA}	25.33 ± 0.83 ^{abA}	21.60 ± 2.80 ^{bA}
SS***	Light	12.97 ± 0.30 ^{aA}	13.60 ± 0.58 ^{aA}	12.97 ± 0.91 ^{aA}
	Dark	12.70 ± 0.25 ^{aA}	13.00 ± 0.93 ^{aA}	13.58 ± 0.44 ^{aA}
pH	Light	5.52 ± 0.16 ^{aA}	5.60 ± 0.04 ^{aA}	5.45 ± 0.14 ^{aA}
	Dark	5.41 ± 0.12 ^{aA}	5.55 ± 0.02 ^{aA}	5.50 ± 0.05 ^{aA}
Lightness (*L*)	Light	57.56 ± 2.32 ^{aB}	43.10 ± 2.00 ^{bA}	40.71 ± 0.73 ^{bA}
	Dark	52.92 ± 1.12 ^{aA}	49.38 ± 1.75 ^{aB}	49.27 ± 0.92 ^{aB}
Chroma (*C*)	Light	64.36 ± 0.94 ^{aB}	38.88 ± 1.99 ^{bA}	37.60 ± 1.30 ^{bA}
	Dark	60.31 ± 1.86 ^{aA}	45.49 ± 1.01 ^{bB}	45.78 ± 1.21 ^{Bb}
Hue angle (°*H*)	Light	75.00 ± 2.72 ^{aA}	101.69 ± 0.72 ^{bA}	102.37 ± 1,97 ^{bB}
	Dark	74.67 ± 4.05 ^{aA}	95.31 ± 4.17 ^{bA}	93.91 ± 1.77 ^{bA}
Films				
Thickness (mm)	-	-	0,06 ± 0,01 ^{a}	0,05 ± 0,01 ^{a}
UVC T (%)	-	-	23,21 ± 2,36 ^{a}	0,69 ± 0,17 ^{b}
UVB T (%)	-	-	38,48 ± 2,59 ^{a}	0,14 ± 0,07 ^{b}
UVA T (%)	-	-	58,51 ± 2,10 ^{a}	1,30 ± 0,36 ^{b}
Visible T (%)	-	-	79,49 ± 0,95 ^{a}	31,76 ± 1,58 ^{b}
L	-	-	32,47 ± 0,06 ^{b}	45,03 ± 0,38 ^{a}
ΔE	-	-	33,60 ± 0,08 ^{b}	45,14 ± 0,42 ^{a}
WI	-	-	30,47 ± 0,06 ^{b}	43,17 ± 0,32 ^{a}
YI	-	-	48,88 ± 0,48 ^{a}	20,87 ± 0,70 ^{b}


Caracterization
Freestanding Film
Casting
Chitosan
Starch
Plasticizer
TiO2
Film forming dispersion
Dispersion
Immersion
CH/ST
CH/ST/T 1%
Absorbance
Wavelength (nm)
Application study on papaya
UV light
Coating
CH/ST/T 1%
24° day
External appearance
Internal appearance
Control
With TiO2
Protection UV
Quality Maintenance

Highlights

- Cassava starch films containing chitosan and nano-TiO_2 were developed;
- Blend of cassava starch/chitosan (1:1) 1% TiO_2 showed improved features;
- Coated fruits were still marketable after 24 days of storage under cooling;
- Coating containing 1% nano-TiO_2 promoted protection UV in papaya;
- Starch/chitosan (1:1) 1% TiO_2 composite coating can maintain the quality of papaya.

CRediT authorship contribution statement

Francisco Leonardo Gomes de Menezes: Conceptualisation, Methodology, Investigation, Formal analysis, Writing -original draft. **Edna Maria Mendes Aroucha:** Conceptualisation, Supervision, Writing - review & editing. **Adrianus Indrat Aria:** Conceptualisation, Writing - review & editing. **Francisco Klebson Gomes dos Santos:** Conceptualisation, Supervision, Writing - review & editing. **Ricardo Henrique de Lima Leite:** Conceptualisation, Writing - review & editing.

Figure(s) 1

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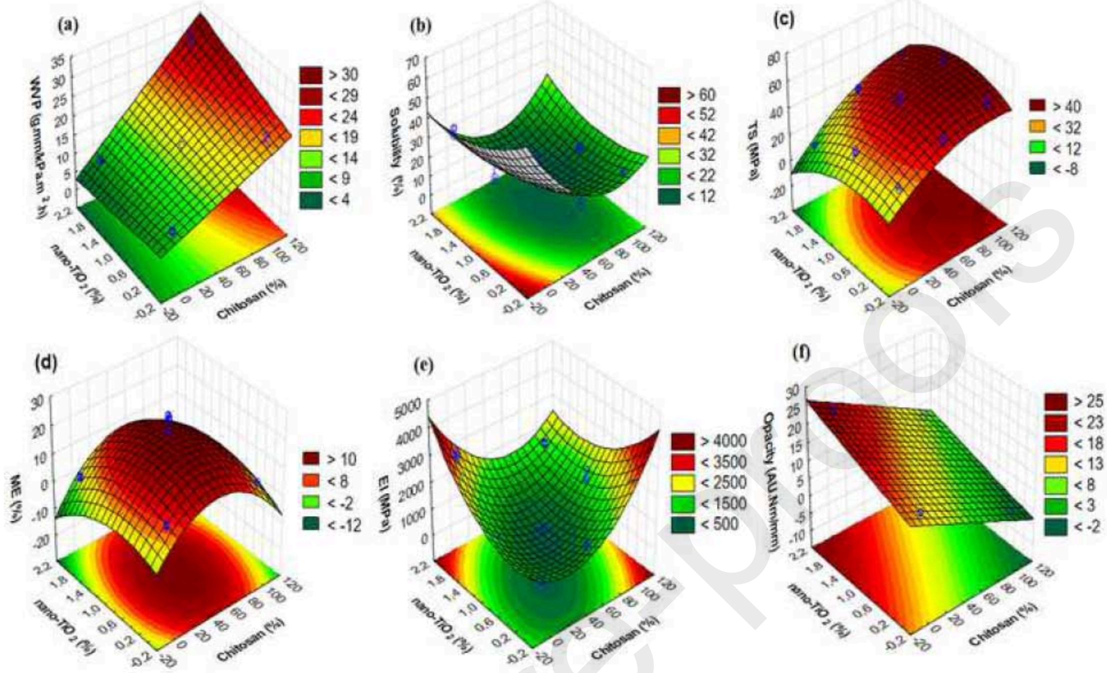

Figure(s) 2

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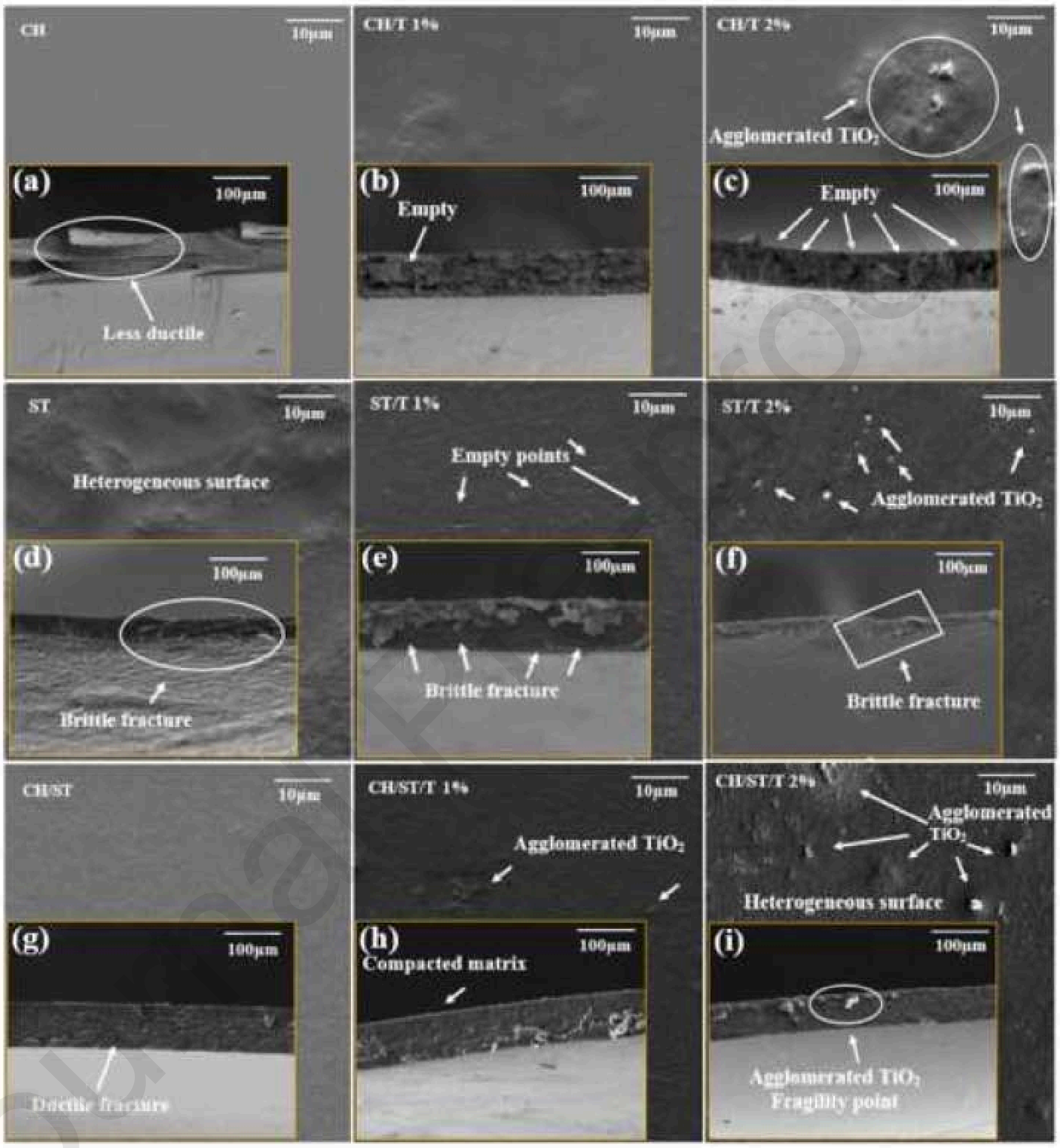

Figure(s) 3

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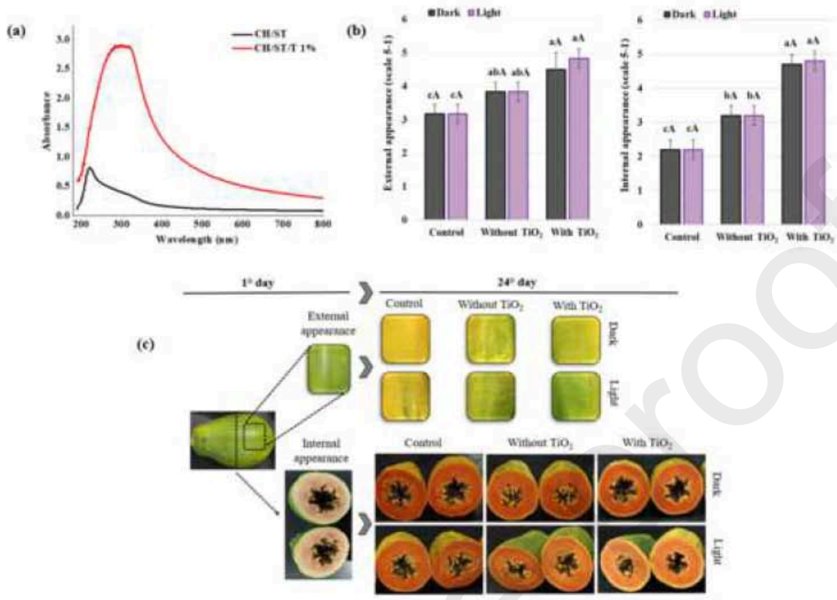

TiO2 incorporated into a blend of biopolymeric matrices improves film properties and affects the postharvest conservation of papaya fruits under UV light

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2024-02-01

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