EFFECT OF MONO AND BILAYER OF CARNAUBA WAX BASED NANO-EMULSION AND HPMC COATINGS ON POST-HARVEST QUALITY OF 'REDTAINUNG' PAPAYA

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Abstract: Coatings are alternatives for post-harvest product conservation since they can provide internal atmosphere changes, reduce moisture loss, and in some cases, act as an antimicrobial agent. This work aimed to evaluate an experimental carnauba wax nanoemulsion coating effects on papaya for postharvest fruit quality. Experimental testes were realized with 'Red Tainung' papaya at USDA-ARS-Florida-USA. Six treatments were applied : i) fruits were coated with single layer of HPMC (hydroxy methyl propyl cellulose) at 0.5% (w/v); ii) carnauba wax nanoemulsion coating (CWNE) at 18% (w/v); iii) a composed coating with CWNE and HPMC; iv) bilayer "A" composed by CWNE (first layer) and HPMC (second layer), v) bilayer "B" composed by HPMC+CWNE and vi) fruits coated with water. Weight loss, internal CO_2 and O_2, peel color were evaluated after storage at 20 °C for 6 days. Uncoated fruits and treated with HPMC resulted in the highest weight loss. Fruits treated with bilayer "B" showed the lowest weight loss, however not different to other coatings containing CWNE. There were no differences for peel color. The highest levels of CO_2 were found for fruits treated with bilayer "B" along with the lowest O_2 among the other treatments. Control presented the lowest levels of CO_2 and the highest O_2. The obtained results showed the potential to combine CWNE and HPMC applying monolayer of composed coating or bilayer "B" combination to improve papaya post-harvest quality.

Keywords: internal gas, fruit quality, nanotechnology, edible coatings.

EFEITO DE MONO E BI-CAMADAS DE REVESTIMENTO A BASE DE NANOEMULSÃO DE CERA DE CARNAÚBA E HPMC NA QUALIDADE PÓS-COLHEITA DE MAMÕES 'REDTAINUNG'

Resumo: Revestimentos são alternativas para a conservação de produtos pós-colheita, pois podem modificar a atmosfera dos frutos, reduzir a perda de umidade e atuar na redução de doenças pós-colheita. O objetivo deste trabalho foi avaliar os efeitos de um revestimento experimental a base de nanoemulsão de cera de carnaúba na qualidade pós-colheita de mamões. Seis tratamentos foram aplicados em mamões 'Red Tainung' no USDA-ARS-Florida, EUA, sendo eles: i) frutos tratados com monocamada de HPMC a 0,5% (p/v); ii) monocamada de nanoemulsão de cera de carnaúba (CWNE) a 18% (p/v); iii) monocamada de revestimento preparado com CWNE e HPMC; iv) bicamada A composta por CWNE (primeira camada) e HPMC (segunda camada); v) bicamada B composta por HPMC seguido de CWNE e vi) frutos revestidos com água destilada. Perda de massa, níveis internos de CO_2 e O_2, coloração da casca foram avaliadas após armazenamento a 20 ° C por 6 dias. Mamões sem revestimento e tratados com HPMC apresentaram maior perda de peso. Frutos tratados com bicamada B apresentaram menor perda de peso, porém não diferiram de outros revestimentos contendo CWNE. Não houve diferenças significativas para coloração da casca. Os maiores níveis de CO_2 foram encontrados nos tratados com bicamada B, juntamente com os menor níveis de O_2 interno entre os tratamentos. Frutos controle apresentaram os menores níveis de CO_2 e maior O_2. Os resultados obtidos mostraram potencial para manutenção da qualidade pós-colheita de mamões ao combinar nanoemulsão de cera de carnaúba e HPMC aplicando monocamada aos frutos ou combinado estes revestimentos na forma de bicamada.

Palavras-chave: composição gasosa interna, qualidade pós-colheita de frutas e hortaliças, nanotecnologia, revestimentos comestíveis.

1. Introduction

Papaya fruit is economic important to Brazil, exported to North American and European markets. Nevertheless, this fruit has a short shelf-life due to high weight loss, rapid ripening and accelerated senescence and susceptible to post-harvest diseases (SINGH, 2010).

Coatings are alternatives for post-harvest product conservation, since they can provide internal atmosphere changes, reduce moisture loss, and in some cases, act as an antimicrobial agent. Therefore, the development and application of protective coatings are being recognized as an alternative and efficient post-harvest technology for fruit preservation (ASSIS; BRITTO, 2014). Coatings act basically by creating a barrier between the fruit and the external environment (BALDWIN et al., 1994).

Lipidic materials are commonly used due their good water barrier properties. On the other hand, polysaccharides, such as hydroxy methyl propyl cellulose (HPMC), demonstrate good film-forming characteristics and have been frequently used as oxygen barriers (OSORIO et al., 2011). Carnauba wax itself (which microstructure allows opaque coating appearance) has been largely used to form conventional coatings and usually is mixed with other waxes, resins and solvents, changing its permeability and resulting in a shiny coating, which is visual attractive to fruits and vegetables, such as citrus for example (PUTTALINGAMMA, 2014; KUMAR; KAPUR, 2016; DE FREITAS et al., 2019).

Therefore, an experimental carnauba wax nanoemulsion was developed using carnauba wax type 1, palm oleic acid and ammonium hydroxide (without to add any other resin, wax or additive) which resulted in a nanostructured coating composed by nanodroplets of lipids that allows great shine. This experimental carnauba wax nanoemulsion have not been extensively explored for postharvest coatings alone or in combination with HPMC to maintain fruit quality and delay fruit ripen and decay.

The aim of this work was to evaluate the effects of an experimental carnauba wax nanoemulsion and HPMC coatings in single layer or in bilayers combination on papaya postharvest fruit quality.

2. Material and Method

2.1. Coatings preparations

2.1.1. Carnauba wax nanoemulsion (CWN)

CWN coating, was prepared with a oil phase composed for carnauba wax type 1 (8 to 18% wt/v), and oleic acid (2.6 to 6% wt/v), from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The water phase was composed of ammonium hydroxide (1 to 3% wt/v), and dimethylpolysiloxane (0.02 to 0.1% v/v) purchased from Sigma-Aldrich Chemical Co. and deionized water (71 to 89% wt/v). A nanoemulsion was accomplished by the inversion phase of W/O to O/W system, using the morpholine-free method proposal by Hagenmaier and Baker (1997) to obtain a microemulsion, with modifications for this work to obtain nanoemulsion. The carnauba wax nanoemulsion diameter size obtained was 44.1 ± 7.6 nm, with a narrow polydispersion index (0.28) and zeta potential -43.8 mV (Miranda, 2015), measured by Zetasizer Nano ZS (Malvern Instruments Inc., Westborough, MA, USA).

2.1.2. Hydroxypropyl methyl cellulose coating (HPMC)

The amount of 0.5 g of HPMC (Sigma Aldrich- viscosity 40-60 cP) was dispersed in 100 mL of hot water at 80 °C at 200 rpm. Then, suspension was cooled to 22 °C remaining overnight under mechanical stirring. No plasticizer was required to this formulation.

2.1.3. Carnauba wax nanoemulsion containing HPMC

Under mechanical stirring, the amount of 0.5 g of HPMC was dispersed in 100 mL of carnauba wax nanoemulsion and remaining overnight under agitation.

2.2. Papaya fruit coating

'RedTainung' papaya (*Carica papaya L.)* from Guatemala were purchase at Nelson´s Family in Homestead-FL at the first maturity stage, with 10% yellow peel color and transported to ARS Horticultural Research Laboratory- Fort Pierce-FL. The fruit was selected, washed and sanitized by immersion in 200 mg L^{-1} peroxyacetic acid during 3 min, air-dried and coated. Sanitized papayas were coated spreading 2 mL of filmogenic solution on the fruit with latex gloves. The coated surface was air-dried at room temperature. The fruits were stored at 22 °C with 80% relative humidity (RH) for 6 days.

Coatings treatments were: i) fruits coated with single layer of HPMC at 0.5% (w/v); ii) carnauba wax nanoemulsion coating (CWNE) at 18% (w/v); iii) a composed coating with CWNE and HPMC; iv) bilayer "A" composed by CWNE (first layer) and HPMC (second layer), v) bilayer "B" composed by HPMC+CWNE and vi) fruits coated with deionized water.

For bilayer treatments, the second layer was applied only after the first layer exhibited to be completely dried. Experiments were conducted in a completely randomized factorial design. Each treatment was performed in triplicate. Determination of percentage of weight loss, internal carbon dioxide (CO_2) and oxygen gas (O_2), peel color (lightness, chroma and hue) were analyzed.

2.3 Postharvest analyzes

2.3.1. Weight loss percentage

Determined in a digital balance, model Marte AS 2000C. The same fruits per treatment were individually measured to calculate water loss.

2.3.2. Internal carbon dioxide (CO_2) and oxygen gas (O_2)

Three fruit samples from each treatment were analyzed by withdrawing an aliquot with 10 mL syringe from the central cavity of the fruit. The CO_2 and O_2 concentration were determined by a same model GC fitted with a CTR column and a thermal conductivity detector. The gas flow rate for helium and air will be 80 and 350 mL· min-1, respectively. Temperatures of oven, injector, and detector will be 70, 250, and 250 °C, respectively

2.3.3. Peel color

Color was measured with a colorimeter Minolta® CR-400 Chroma Meter (Minolta Camera Co., Osaka, Japan), using the CIELAB system: L* (lightness), a* and b* values (McGUIRE, 1992). The instrument was calibrated using a standard white reflector plate. Values were obtained from the same fruits per treatment and three determinations for each fruit.

3. Results and Discussion

Table 1 shows weight loss, lightness, chroma and hue angle of 'RedTainung' papaya fruit.

Uncoated fruits and treated with HPMC resulted in the highest weight loss. Fruits treated with bilayer B showed the lowest weight loss, however not different to other coatings containing CWNE. Lipid-based coatings, such as carnauba wax, are more hydrophobic and expected to act effectively as moisture (ASSIS et al., 2008; LIN; ZHAO, 2007). HPMC coating due to its hydrophilic characteristic allows water vapor loss.

Carnauba wax was efficient to reduce water loss typical to this hydrophobic coating (BALDWIN et. al, 1999) and showed to be an appropriated barrier to decrease water loss (KIM et al., 2014; JO et al., 2014).

There were no differences for lightness and chroma among treatments. However, control showed the lowest value for hue angle (closer to the orange color angle); followed by the other treatments which showed intermediate values, excepted for fruits treated with a single layer of CWNE which showed the highest value (closer to the green color angle). Fruits treated with a single layer of CWNE coating remain the green color peel longer than the other treatments.

Table 1. Weight loss, lightness, chroma and hue angle of ‘RedTainung’ papaya fruit coated with different coatings and stored at 20 °C for 6 days.

Treatments	Weight loss	Ligthness	Chroma	Hue angle
Control	10.9 ± 0.3 a	57.3 ±1.2 a	45.2 ± 1.8 a	82.7 ± 5.0 b
SL HPMC* 0.5 %	10.7 ± 3.4 a	57.3 ± 4.0 a	48.2 ± 3.8 a	86.4 ± 5.1 ab
SL CWNE** 18%	3.2 ± 0.8 b	54.0 ± 2.0 a	43.2 ± 3.4 a	93.6 ± 1.3 a
SL CWNE with HPMC	3.0 ± 1.3 b	54.3 ± 2.1 a	44.3 ± 2.8 a	87.7 ± 6.5 ab
BL CWNE+HPMC	3.1 ± 0.4 b	53.3 ± 2.1 a	42.5 ± 2.3 a	89.2 ± 8.4 ab
BL HPMC+CWNE	2.8 ± 0.8 b	55.3 ± 2.1 a	45.9 ± 3.7 a	87.9 ± 4.2 ab

*SL: single layer; BL: bilayer. Average ± Std. Deviation, *hydroxypropyl methylcellulose coating; **Carnauba wax nanoemulsion coating. Columns with different letters are significantly different by Duncan test ($p<0.05$) applied after ANOVA*

Internal dioxide carbon (CO_2) generally increased and oxygen gas (O_2) decreased during storage. Control presented the expected internal gaseous composition, with the lowest levels of CO_2 and highest O_2. The highest levels of CO_2 were found for fruits treated with bilayer “B” (BL-HPMC+CWNE) along with the lowest O_2 among the other treatments. CWNE coating was less permeable to CO_2, since the fruits coated with this lipid presented higher level dioxide carbon than uncoated or fruits treated with only HPMC. However, bilayer coating constituted for the combination HPMC followed for CWNE showed less permeability to CO_2 than bilayer composed for the opposite combination (CWNE followed by HPMC), Figure 1.

Related to the O_2, HPMC coating exhibited more permeable than CWNE. Fruits coated with carnauba wax nanoemulsion showed a lower level of internal oxygen gas after 6 days of storage at 20 °C.

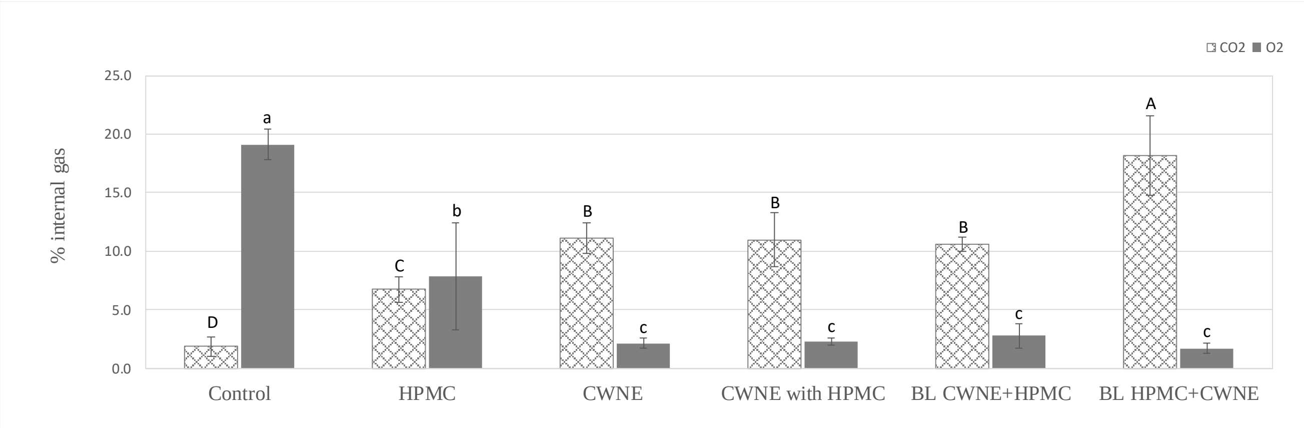

Figure 1. Internal gas (CO_2 and O_2) of ‘RedTainung’ papaya fruit coated with different coatings and stored at 20 °C for 6 days. Columns with different Uppercase letters are significantly different by Duncan test ($p<0.05$) applied after ANOVA. The same rule apply to lowercase letters. BL: bilayer.; HPMC: hydroxypropyl methylcellulose coating; CWNE: carnauba wax nanoemulsion coating

4. Conclusions

Carnauba wax nanoemulsion coating showed more suitable to reduce the internal level of oxygen gas and rise up dioxide carbon gas levels on papayas than HPMC. The use of this coating by itself or in bilayer combination CWNE and HPMC composed first for HPMC followed by CWNE showed potential to maintain papaya post-harvest quality. Sensory analyses need to be done to verify the levels of ethanol in each treatment which may add undesirable flavor to the fruits.

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