BIOPLASTICS MADE UP OF FRUIT PUREES

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Abstract – Edible films have been widely studied as sustainable alternatives to replace petroleum-based materials and provide food packaging with innovative sensory and nutritional attributes. We have developed edible films based on passion fruit, red guava, and watermelon by using a pilot scale casting approach. Pectin (5 wt.%) and glycerol (30 wt.%) were used as matrix component and plasticizer, respectively. Color analyses showed that fruit purees' color was retained in their resulting films after casting at 120 °C. Fruit puree films showed plastic behavior with tensile strength and elongation at break varying between 0.8 MPa - 2.0 MPa, and 8 % - 15 %, respectively. Tensile tests also confirmed that tensile properties of fruit puree-based films are relative humidity (RH) dependent. A comparison regarding mechanical performance and water affinity for the as-developed fruit puree films is further reported.
Keywords: *edible film; food packaging; nutritional attributes; mechanical properties; nanoscience.*

Introduction

Innovative concepts have been explored throughout the past decades aiming at developing sustainable food packaging with unique characteristics and functions. Edible films, for instance, have been widely studied to replace petroleum-based materials and provide novel edible packaging without any health concerns, while also being biodegradable and obtained from renewable sources. Our group pioneered the production of fruit puree-based edible films with novel sensory and nutritional attributes. In 1996, Tara McHugh, the leading scientist of this research, reported the first edible films based on peach, apricot, apple, and pear [1]. Since then, we have been investigating several natural polymers (e.g., pectins, starches, alginates, gelatins, and cellulose derivatives) as well as many plant sources to produce edible films with desirable color, and flavor. These include acai, acerola [2], apple, guava [3], papaya [4], strawberry, and tomato. Our group has also been developing fruit puree-based nanocomposite films aiming at matching the mechanical and barrier properties of synthetic polymer-based packaging. Previous studies on chitosan nanoparticles [3] and cellulose whiskers have been used in that regard. In addition, we have incorporated bioactive substances (e.g., plant essential oils and their active compounds) to provide the edible films with antimicrobial properties to extend food shelf life and ensure food safety [4]. As fruit puree-based edible films have recently boomed in popularity within academia and research institutes, our group has been continuously expanding our research scope by moving towards the use of fruits and vegetables in an "as natural as possible" manner by formulating edible films with the whole fruit, including seeds. Here, we report the development of new edible films from red guava, passion fruit, and watermelon purees through a continuous casting method. This work characterized the colorimetric, mechanical and water affinity properties of these fruit puree-based edible films.

Experimental

Materials: Crimson sweet watermelon (WM), red guava (RG), and golden passion fruit (PF), were purchased from a local market. Low-methoxyl pectin (LM-PEC) (M_w = 170,000 g mol^{-1}) was purchased from CPKelco. Glycerol was purchased from Synth. Ultra-pure H_2O (ρ = 18.2 MΩ cm) obtained with a Milli-Q system (Barnstead Nanopure Diamond) was used in all experimental procedures.

Preparation of fruit puree-based films: 150 g of freshly prepared fruit puree was mixed with 150 g of water. To this mixture we added pectin (5 %, $m_{\text{LM-PEC}}\ m_{\text{mixture}}^{-1}$) and glycerol (30 %, $m_{\text{glycerol}}\ m_{\text{LM-PEC}}^{-1}$). The resulting formulation was homogenized for 10 min with a MA102 homogenizer (Marconi, Brazil). Fruit puree formulations were cast by a continuous transport approach using a KTF-B Mathis Labcoater unit (Werner Mathis AG, Switzerland) (Fig. 1). The wet layer thickness was controlled at 0.18 – 0.25 mm using a doctor knife type B. In a typical casting process, the wet layer was first heated by conveying through an infrared (IR) predryer with IR radiators potency adjusted to 40-50 %, and then conveyed through a convective drying oven running at temperature of 120 °C (Fig. 1a). At the outlet the dried film was rolled up automatically, and stored for further characterizations (Fig 1b). Fruit puree formulations were continuously processed at rolling speed of 0.12 m min^{-1}, which led to film formation in 4 min.

Analysis of color: Color parameters (CIELab scale) of film-forming solutions (FFS) and dried films were determined using a CR-400 Chroma Meter (Konica Minolta Sensing, Inc., Osaka, Japan). Luminosity ($L*$), red-green ($a*$) and yellow-blue ($b*$) parameters were calculated as the average of three random measurements. Color change throughout drying was quantified by total color difference (ΔE), calculated as $\Delta E = [(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2]^{0,5}$, where $\Delta L* = L*_{solution} - L*_{film}$, $\Delta a* = a*_{solution} - a*_{film}$, and $\Delta b* = b*_{solution} - b*_{film}$. Yellowness index ($YI$) and whiteness index ($WI$) were calculated as $YI = 142.86 \cdot b* \cdot L*^{-1}$ and $WI = 100 - [(100 - L*)^2 + a*^2 + b^2]^{0,5}$, respectively.

Mechanical tests: Uniaxial tensile tests were carried out at 24 °C in an EMIC DL3000 Universal Testing Machine (EMIC Equipamentos e Sistemas de Ensaio LTDA, Brazil) following the ASTM D882-09 protocol. Stress-strain curves were recorded for Type I specimens (Fig. 1c) using a crosshead speed of 5 mm min^{-1}. Samples were conditioned at relative humidity of 50 ± 3% and 75 ± 3 % in order to examine the hydration level dependence of tensile properties.

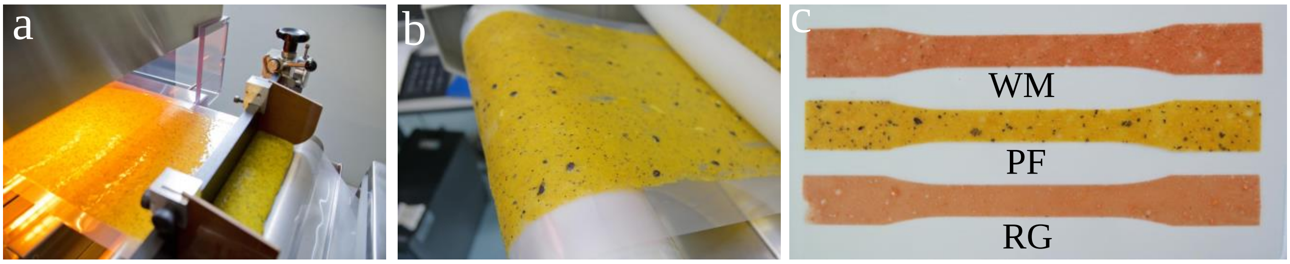

Figure 1: Illustrative photographs of continuous casting process for obtaining of fruit puree films. (a) Coating device, doctor knife type B, and IR predryer; (b) Rolling device and final fruit puree film; (c) Corresponding type I specimens for red guava (RG)-, passion fruit (PF)-, and watermelon (WM)-based films.

Water uptake determinations: The water uptake was determined gravimetrically by introducing film samples previously dried at 50 °C for 48 h into desiccators equilibrated at RH of 50 % and 75 %. After 48 h, samples were removed from the desiccators and immediately weighed (± 0.0001). Water uptake was calculated as being: w_u ($g_{H_2O}\ g_{film}^{-1}$) = $(m_f - m_o)/m_o$, where m_f and m_o are the mass of swollen and dry films, respectively. Water uptake determinations were performed in triplicate.

Water solubility tests: The water solubility of fruit puree films was estimated according to literature (LOREVICE et al. 2012). Film samples previously dried at 100 °C for 2 h were immersed into 30 mL of deionized water, and gently stirred at 27 °C for different time intervals. Samples were then filtered to separate the solubilized portion, and finally dried at 100 °C for 12 hours. Water solubility was calculated as being: w_s (%) = $[(m_i - m_f)/m_i] \times 100$, where m_i is the initial film mass and m_f is the dried film mass after water immersion.

Results and discussion

The colorimetric parameters *L**, *a**, and *b** as well as yellowness and whiteness indices of the FFS and fruit-puree films are presented in Table 1. As seen in Table 1, PF-containing FFS showed the highest *L** value, followed by RG and WM. This behavior was also observed for dried films. *L** value, also known as lightness, ranges from 0 (black) to 100 (white). Thus, WM-based FFS and WM-film were the darkest samples among these three fruits, whereas PF-based FFS and PF-film were the lightest ones. Regardless of the formulation, dried films were lighter than their corresponding FFS as indicated by higher *L** values.

Table 1: Colorimetric parameters (*L, *a**, and *b**), yellowness index (*YI*), and whiteness index (*WI*) of passion fruit (PF)-, red guava (RG)-, and watermelon (WM)-based edible films and film-forming solutions (FFSs).**

Type of sample	Parameter	Passion fruit (PF)	Red Guava (RG)	Watermelon (WM)
Film-forming solution	L^*	43.40 ± 0.59^{d}	37.49 ± 0.11^{b}	34.64 ± 0.12^{a}
	a^*	-0.65 ± 0.06^{2}	10.58 ± 0.04^{6}	8.21 ± 0.08^{4}
	b^*	22.09 ± 0.59^{F}	9.05 ± 0.05^{BC}	8.82 ± 0.08^{B}
	YI	$72.71 \pm 1.02^{\varepsilon}$	$34.50 \pm 0.19^{\gamma}$	$36.36 \pm 0.47^{\gamma}$
	WI	76.65 ± 0.55^{A}	$83.98 \pm 0.05^{\Delta}$	85.49 ± 0.09^{E}
Puree fruit film	L^*	48.88 ± 0.38^{g}	46.58 ± 0.23^{f}	44.82 ± 0.55^{e}
	a^*	3.91 ± 0.04^{3}	11.70 ± 0.02^{7}	9.90 ± 0.21^{5}
	b^*	17.75 ± 0.29^{E}	11.74 ± 0.05^{D}	9.55 ± 0.13^{C}
	YI	$51.88 \pm 1.15^{\delta}$	$36.00 \pm 0.23^{\gamma}$	$30.45 \pm 0.22^{\beta}$
	WI	80.47 ± 0.27^{B}	$81.88 \pm 0.04^{\Gamma}$	$84.36 \pm 0.08^{\Delta}$

$^{a-g}$ *L** values followed by the same superscript lowercase letters are not different ($p > 0.05$);
$^{1-7}$ *a** values followed by the same superscript Arabic numerals are not different ($p > 0.05$);
$^{A-F}$ *b** values followed by the same superscript uppercase letters are not different ($p > 0.05$);
$^{\alpha-\varepsilon}$ *YI* values followed by the same superscript lowercase Greek letters are not different ($p > 0.05$);
$^{A-Z}$ *WI* values followed by the same superscript uppercase Greek letters are not different ($p > 0.05$).

Negative *a** values indicate a green color whereas positive *a** values are related to red color. As expected, RG- and WM-based FFSs and edible films showed higher *a** values than the PF-containing ones ($p < 0.05$). This is attributed to their natural reddish appearance. Regardless of the formulation, films were redder than FFSs as indicated by higher ($p < 0.05$) *a** values. This outcome may be a result of the concentration of chromophoric groups upon water evaporation during film formation by continuous casting. Negative *b** values are related to a blue color while positive *b** values indicate a yellow color. As expected, *b** was higher ($p < 0.05$) for PF-based films and FFSs as a result of PF's natural yellowish appearance. This was confirmed by the higher ($p < 0.05$) *YI* these samples. Film drying reduced ($p < 0.05$) *YI* of PF- and WM-based FFSs, but not that of RG. *WI* was also reduced ($p < 0.05$) for RG- and WM-based samples, but not for PF ones. ΔE quantifies the color changes as a result of film drying by comparing the color parameters measured both on films and FFSs. PF-, RG-, and WM-based samples showed ΔE values of 8.37 ± 0.32, 9.54 ± 0.28, and 10.35 ± 0.50, respectively. The last two values were not statistically different ($p > 0.05$) and were higher ($p < 0.05$) than the first one. For comparison purposes, FFSs' ΔE values were also determined for a blank standard (*L**:97.46, *a**: -0.11, *b**: 1.92). The values were 57.70 ± 0.35, 61.33 ± 0.10, and 63.74 ± 0.14, respectively. As ΔE values were remarkably lower for film drying, one may conclude that the continuous casting process maintained a desirable fruit color.

Elastic Modulus (E), tensile strength (σ_T), and elongation at break (ε_B) of the fruit puree films exposed to different relative humidity are reported in Table 3. For 50 % RH, WM-, RG- and PF-based films were found to possess σ_T in the range 1 MPa – 2 MPa. WM films exhibited the lowest σ_T, while RG-films showed the highest σ_T among the as-made fruit puree films. Conversely, all fruit puree films were found to be much flexible at higher RH, as expressed by their greater ε_B values. It was also noted that ε_B values for WM, RG, and PF films were similar ($p > 0.05$), suggesting that the flexibility of these films, in particular, may have been determined by glycerol content rather than the type of fruit puree.

Table 3: Mechanical data for fruit puree-based plastics obtained by continuous casting*

Sample	***E* (MPa)**		**σ_T (MPa)**		**ε_B (%)**	
	50 % RH	**75 % RH**	**50 % RH**	**75 % RH**	**50 % RH**	**75 % RH**
WM	$139 \pm 46^{a,1}$	$7 \pm 0.4^{b,1}$	$1.2 \pm 0.3^{a,1}$	$0.9 \pm 0.2^{b,1}$	$12.0 \pm 1.9^{a,1}$	$15.3 \pm 0.7^{b,1}$
RG	$21 \pm 9^{a,2}$	$19 \pm 1^{a,2}$	$2.0 \pm 0.1^{a,2}$	$1.6 \pm 0.1^{b,2}$	$10.2 \pm 1.0^{a,1}$	$14.3 \pm 2.0^{b,1}$
PF	$36 \pm 8^{a,2}$	$12 \pm 2^{b,3}$	$1.6 \pm 0.3^{a,1}$	$0.8 \pm 0.1^{b,1}$	$8.9 \pm 1.0^{a,1}$	$13.2 \pm 2.3^{b,1}$

*ANOVA: Mean value ± standard deviation. Values in the same row bearing the same letter, and values in the same column bearing the same number are not significantly different ($p > 0.05$) according to Tukey's test.

It should be expected that fruit puree-based films could behave mechanically depending on some physical-chemical aspect of their original fruit. We have used higher hydration levels, by conditioning samples at 75 % RH, as a way to access this. It was noted that $\boldsymbol{\varepsilon_B}$ significantly increased at higher RHs for all film samples ($p < 0.05$). This was likely because of more effective plasticization of films due to higher amount of water absorbed at 75 % RH. Additionally, it is worth mentioning differences in stiffness between the WM-, RG- and PF-based films. While E of the RG-film did not change when RH was increased ($p > 0.05$), E values for WM and PF films decreased significantly ($p < 0.05$). Such decreases in E indicates higher water uptake for these samples compared with RG-films.

Water uptake for samples conditioned at 50 % and 75 % RH for 48 h (equal conditioning time used in mechanical tests) was examined, and data have been summarized in Table 4. It can be verified that fruit puree films absorbed equivalent amounts of water both at 50 % and 75 % RH, but WM-film swelled to a slightly greater extent than RG- and PF-films.

Table 4: Water uptake and solubility data for fruit puree-based bioplastics

Sample	**Water Uptake ($g_{H2O}\ g_{film}^{-1}$)***		**Water Solubility (%)**		
	50 % RH	**75 % RH**	**5 min**	**10 min**	**1200 min**
WM	0.125 ± 0.003^{a}	0.277 ± 0.008^{b}	38.2	54.1	61.7
RG	0.118 ± 0.001^{a}	0.254 ± 0.006^{b}	43.2	63.3	81.3
PF	0.102 ± 0.004^{a}	0.230 ± 0.014^{b}	51.2	50.0	82.4

*ANOVA: Mean value ± standard deviation. Values in the same row bearing the same letter are not significantly different ($p > 0.05$) according to Tukey's test.

Water uptake data suggest that variations in mechanical properties of fruit puree films with increasing RH were a result of structural changes in films caused by different levels of swelling rather than amount of water itself. As WM and PF are very hydrated fruits, the high swelling capacity of their pulpy fibrous structures may have led their corresponding films to weaken at moderate humidity conditions. In this sense, the microstructure of RG-film was found to be influenced to the lowest extent by RH.

Preliminary water solubility (w_s) results for the film samples have also been summarized in Table 2. It can be noticed that WM-, PF-, and RG-films were rapidly dissolved after immersion into water, as they lost nearly 50 wt.% of their mass within 5 min. The high w_s of fruit puree films was possibly caused by their high concentration of soluble compounds, such as glycerol and pectin used in the film-forming mixtures, and other sugars naturally occurring in fruit purees [5]. The solubility of fruit puree films was visually confirmed after 1200 min by the formation of homogeneous suspensions. Water solubility is an important parameter, and can determine the performance of fruit puree films in various applications. Thus strategies aiming at controlling water solubility of edible films have been recently proposed by our research group. For instance, Lorevice et al. (2012) reported improvements on water solubility of guava puree/hydroxypropyl methylcellulose films through the addition of chitosan nanoparticles [3]. More recently, the use of essential oil nanoemulsions was also reported by Moura et al. (2014) as a way to reduce water solubility of pectin-based films [6]. Nanoscience techniques could also be used to reduce water solubility of the WM-, PF- and RG-films developed in the present work. This subject matter will be addressed in future reports.

Conclusion

New edible films based on red guava, watermelon and passion fruit have been successfully developed by a pilot scale casting method. Pectin was used as a matrix component and glycerol was used as a plasticizer. Fruit color was suitably maintained after continuously casting the solutions into films. The materials showed plastic behavior with tensile strength and elongation at break varying between 0.8 MPa - 2.0 MPa, and 8 % - 15 %, respectively. The mechanical performance of these fruit puree-based films was confirmed to be dependent on RH. Rapid water solubility was also confirmed for all films. This behavior can be utilized to guide application of these edible bioplastics in various food packaging sectors.

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