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Developments of biodegradable polymer based on polylactic acid (PLA) with natural color extracts for packaging film applications

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Abstract

This research was interested in the use of natural colorants to replace hazardous synthetic pigments in the plastic polymer industry. The natural colors were selected from local plants indigenous to southeast Asia, which were *Hibiscus sabdariffa* roselle calyx (RS) and *Caesapinia sappan* Linn heartwood (SP). Natural colorant extracts were used as additives in poly(lactic acid) (PLA). These were manufactured using a twin screws extruder and blow film extruder to obtain biodegradable thin films for use as packaging materials. Biodegradable films were characterized by color index, light barrier properties, water vapor transmission (WVTR), morphology, mechanical and chemical properties. The results showed high compatibility between PLA and natural color extracts confirmed via SEM morphology. Moreover, the films have the colors associated with the added RS and SP extracts, with a pink tone for the RS film and a yellow-orange tone for the SP film. Films incorporated with the extracts also possessed improved light barrier properties, which were reduced from 98.66% to 78.00% in the UV-A region and 99.33% to 90.00% in the visible region. Water vapor transmission rate was also decreased with incorporation of SP from 4.02 $g \cdot m^{-2} * day$ to 2.98 $g \cdot m^{-2} * day$ at 7 days and RS 1.66 $g \cdot m^{-2} * day$ to 1.59 $g \cdot m^{-2} * day$ at 14 days. Moreover, films containing the natural color extracts had higher tensile strength and tensile modulus than pure PLA films. These properties improvement confirm that these extracts are suitable for producing biodegradable packaging thin films.

1. Introduction

Polymeric films are widely used in various applications ranging from simple packaging to medical devices [1]. The largest use of polymer films by weight is in the packaging industry. Generally, plastic packaging films are produced from petroleum-based resources such as polyethylene (PE), polypropylene (PP) and poly(ethylene terephthalate) (PET). One major problem with packaging films is their short lifecycle, a solution to this problem is recycling however, this is often cost prohibitive. Therefore, the majority of films end up in landfills or burnt generating waste and releasing toxic chemicals that contaminate the environment [2]. Thus, due to greater environmental concerns there is a drive to use bio-based and/or biodegradable polymers such as poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) [3,4]. However, the performance of film produced from these polymers needs to be improved for packaging films and therefore additives are usually incorporated. These additives tend to include processing agents, plasticizers and pigments [5].

Pigments or dyes are additives used to improve the product color, price and barrier properties [6]. However, synthetic dyes and pigments are traditionally prepared from toxic substances such as heavy metals that can be subsequently released from the product.

Natural pigments are an alternative for synthetic dye-pigments. Natural colorants can be applied within many applications because of their inherent good properties such as; light barrier properties, plasticizing ability, antioxidant, antimicrobial activity, and also potential indicating properties. Various parts of plants such as the bark, leaves, flowers, fruits, calyx, heartwoods, peels can be selected and extracted in order to obtain natural dye-pigments [7-9] . Previous research has seen various examples such as, composite packaging preparation by sappan heartwood compound with PLA [10], and roselle extraction mixed with biodegradable polymers such as starch/PVA [11,12], PVA/chitosan [13], for intelligent packaging were reported. In general, natural color compounds are applied to packaging products using a casting method that has low productivity in industrial manufacturing.

This research focuses on two natural colorants: *Caesalpinia sappan* L. (sappan) heartwood and *Hibiscus sabdariffa* L. (roselle) calyx. These two natural colorants possess flavonoids as the main group of compounds in sappan heartwood and roselle calyx. Sappan is a plant that has been applied in many areas such as traditional medicine, food and beverage, pharmaceutical, dyeing and cosmetics. A red color tone is generally obtained from the sappan heartwood extract, which arises from the conversion of the major compound constituent brazilin to brazilein [10] . Similarly, roselle is a plant that is found around the world and is widely grown throughout southeast Asia countries such as Thailand. The flavonoid anthocyanin is the major component

in roselle calyx and is also pH sensitive. Generally, the red color of roselle results from the anthocyanin changing its chemical structure to a flavylium structure [14].

The purpose of this research was to prepare biodegradable packaging films based on poly(lactic acid) (PLA) with roselle calyx and sappan heartwood extracts used as additives within the PLA film. These films are first produced by a twin-screws extruder and then a blow film extruder. These processing techniques allow for this to be scaled up on an industrial scale. The produced films should therefore be non-toxic to humans and environment as during the biodegradation stage non-harmful chemicals are released.

2. Experimental

2.1 Materials

Two natural colorants were chosen; *Hibiscus sabdariffa* L. calyx and *Caesalpinia sappan* L. heartwood which were purchased from a local market in Phitsanulok province, Thailand (Osot-Niyom shop). Polylactic acid (PLA) was purchased from Natural Works LLC, Ingeo™ Biopolymer 4043D (Film grade), Molecular weight is 120,000 g·mol^{-1}, T_g = 60°C to 65°C, T_m = 145°C to 160°C, MFI = 6 g·10 min^{-1}. Commercial grade Ethanol (95%) was bought from Sigma Aldrich (Singapore) that was used for natural colorant extraction.

2.2 Natural color extraction

Dried sappan heartwood was extracted using 80 wt% ethanol with 50 g : 300 mL solid/solvent (ratio 1:6) and kept in the dark at room temperature for 72 h. Afterwards, the solvent was filtered by filter paper and evaporated under reduced pressure by a rotary evaporator (at 60°C, 100 rpm) to produce a red solid crude extract (7% yield (w/w) of dried heartwood). Likewise, dried roselle calyx was pulverized and the dried powder was further extracted using 80% ethanol with 50 g : 750 mL solid/solvent (ratio 1:15) at 50°C for 1 h. The obtained solvent was filtered and evaporated using the same procedure for sappan heartwood extract. A crude roselle calyx extract was obtained as a dark red viscos crude extract with 7% yield (w/w) of dried calyx.

Each of crude extracts was redissolved in 95% ethanol to produce 20%w/v of extract solution and stored at a temperature of 4°C before compounding in PLA preparation process.

2.3 Biodegradable film based-on PLA preparation

Polylactic acid (PLA) was used to prepare a biodegradable packaging film by twin screw extruder and blow film extruder. Twin screw extrusion temperatures (Feeding zone, compression zone and metering zone) were set the at 100, 120, 150, 160, 170, 180, 190, 180°C and blow film extrusion temperatures were 150, 170, 180, and 170°C, respectively [6,18]. PLA was combined with either 20 wt% roselle calyx and sappan heartwood mixture extracts solution at two different contents, 0.1 wt% and 0.2 wt%. Film thickness was controlled at 70 µm and stored at room temperature without moisture and light for 7 days before film characterization.

2.4 Characterization

The melt flow index (MFR) of the PLA/extract compounds were analyzed by melt flow machine following ASTM D1238A, at a temperature of 190°C with a load of 2.16 N. 6 g of compounds was loaded to the melt flow machine and the data was calculated in MFR (g·10 min^{-1}).

The color of the biodegradable packaging films and extruded compounds were measured using a color reader CR-20. Biodegradable packaging films and extruded compounds were measured at 5 points per sample/5 times (n = 5) and the data was averaged and reported as lightness (L), redness (a), yellowness (b) and ΔE following Equation (1).

$$\Delta E = \left[\left(L-L^*\right)^2 + \left(a-a^*\right)^2 + \left(b-b^*\right)^2 \right]^{1/2} \quad (1)$$

Where L is Lightness, a, a^* is redness, b, b^* is yellowness

Scanning Electron Microscope (SEM - LeO1455VP model) was used to measure sample film morphology. the samples surface was fixed onto a metal stub and sputter coated with gold before testing.

The water vapor transmission rate (WVTR) of films was tested by a gravimetric method following ASTM E96-80. The sample size was prepared at a size of 5 cm^2, which was covered with a glass jar containing anhydrous silica gel and the tests were repeated 5 times per sample. The sample films were kept under controlled conditions at room temperature and 55% humidity in a desiccator. The weight change was collected every day for 14 days and the WVTR calculated using Equation (2). [15,16]

$$WVTR = W / (area \times time)\ (g \cdot m^{-2} \cdot day) \quad (2)$$

Where, W is the increased weight of film (g), A is area (m^2), time is day of testing (day)

The light transmittance of sample films was measured by UV-Vis spectrophotometer model SPECORD 200 PLUS. The sample films were prepared in square shape sizes of 5 cm^2 using 5 pieces/sample and a film thickness of 70 µm. The wavelength range was set at 200 nm to 800 nm at room temperature.

Mechanical properties were measured using Universal Testing Machine (Instron 5965) following ASTM D638. The sample films were cut in to a dumbbell shape with 10 pieces per sample. The tested conditions used a gauge length 57 mm, cross ahead speed 200 mm·min^{-1}, load force of 100 N. Each sample film was tested in two directions, machine direction (MD) and transverse direction (TD).

The crystalline structure of sample films was determined by X-ray diffraction (XRD) via an X-ray Diffractometry BRUKER, D2 Phaser. Sample films were prepared in a square shape 5 cm^2. The 2θ detection angle was collected at 5° to 40° at 5°·min^{-1}, with a step of 0.02° [21].

The thermal properties of the films were characterized by differential scanning calorimetry (DSC). Film samples were cut to small pieces weighing 6 mg to 8 mg and placed on the aluminum pan. Temperature conditions was set between 25°C to 250°C, with a heating rate 10°C·min^{-1} in nitrogen atmosphere. The thermal procedure had two heating steps, first heating step 25°C to 250°C, heating rate 10°C·min^{-1} after that the temperature was reduced to 25°C (cooling step) with the same heating rate. Finally, the second heating step heated to the sample

to 250°C at a 10°C·min^{-1} heating rate. Degree of crystallinity was calculated by the following equation [22]. (ΔH^{*}_{m} of neat PLA theory 93.7 J·g^{-1})

$$\%X_c = \left(\Delta H_m / \Delta H_m^*\right) \times 100 \quad (3)$$

3. Results and discussions

3.1 Melt flow index

As the final fabricated biodegradable packaging films will be thermally processed via a twin screw and blow film extruder it is important to understand how the natural extracts influence the flow behavior. Therefore, the PLA/roselle and PLA/sappan compounds were analyzed for the melt flow rate (MFR). Figure 1 presents the MFR of 5 samples, namely, pure PLA and PLA combined with 0.1 wt% and 0.2 wt% of roselle and sappan extract. PLA compound without natural colorant had the lowest MFR (4.74 g·10 min^{-1}) when compared with PLA compounds mixed with natural colorant. when the roselle extract was added to PLA at 0.1 wt% and 0.2 wt% showed a slightly increased in MFR at 4.96 g·10 min^{-1} and 5.18 g·10 min^{-1}, respectively. The roselle extract influences the PLA structure and increases the free volume between the polymer chains and acts as a plasticizer. Similarly, PLA mixed with sappan extract also gave a higher MFR when compared to pure PLA at 5.25 g·10 min^{-1} and 5.02 g·10 min^{-1}. Again it is thought that that the slight improvement transpires from the enhanced polymer chain mobility due to the polyphenolic compounds present in the natural colorant [24,25]. This result is also related to DSC thermogram results in first heat step that is presented in Figure 7.

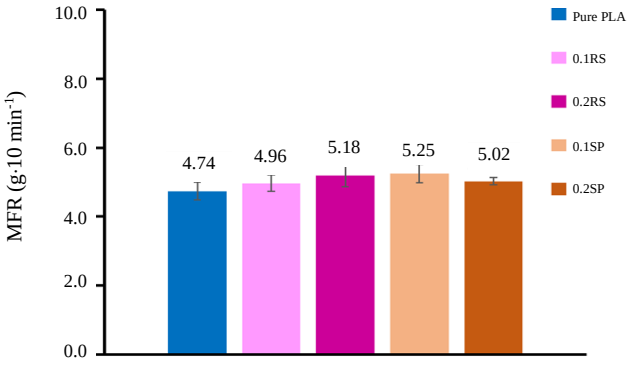

Figure 1. Melt flow rate (MFR) of biodegradable compounded mixed with roselle and sappan extraction.

3.2 Biodegradable films Morphology

The biodegradable film morphology was characterized by SEM technique. Film morphology (cross section) results are depicted in Figure 2, which shows that all sample films possess a different texture. Figure 2(a) pure PLA film cross section depicts a homogenous phase but there are also some unmelted pellets in the PLA phase. After adding the roselle and sappan heartwood extracts (Figure 2(b), 2(c), 2(d) and 2(e), showed different morphologies compared with pure PLA. Films incorporated with different contents of roselle and sappan depicted a homogenous phase and stretches and cracks in PLA matrix. This indicates that the PLA film mixed with natural colorant have high compatibility between the PLA polymer matrix and colorant additive.

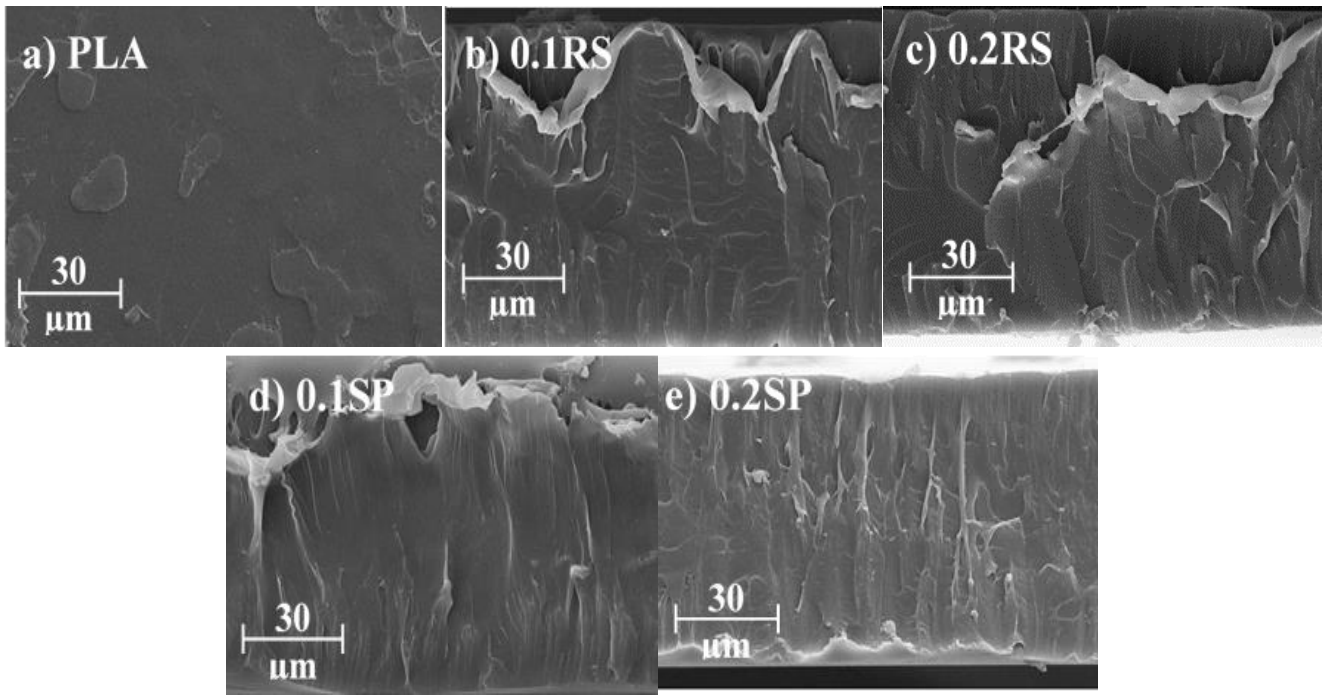

Figure 2. Biodegradable films morphology (cross section) at 1000X magnification a) Pure PLA, b) 0.1RS, c) 0.2RS, d) 0.1SP, e) 0.2SP.

Table 1. Color parameter index of biodegradable films.

Sample	L	a	b	ΔE
Pure PLA	87.80 ± 0.26	-0.70 ± 0.00	-4.26 ± 0.05	Ref
0.1RS	87.56 ± 0.25	-0.70 ± 0.00	-4.16 ± 0.05	0.34 ± 0.06
0.2RS	87.24 ± 0.05	-0.60 ± 0.00	-3.96 ± 0.05	0.64 ± 0.05
0.1SP	87.06 ± 0.13	-1.26 ± 0.05	-0.20 ± 0.10	4.16 ± 0.010
0.2SP	86.78 ± 0.20	-1.86 ± 0.05	3.52 ± 0.18	7.93 ± 0.018

Next the color parameter index of the PLA based biodegradable films was determined by a color reader. Table 1, shows the color results in terms of L (lightness-darkness), a (redness-greenness), b (yellowness-blueness). Pure PLA film present a high value of lightness at 87.80 when compared with biodegradable film incorporated with natural colorant (roselle and sappan) which show a slight reduction in film lightness. In terms of redness (a) and yellowness (b) values, these show higher redness values with higher content of roselle and sappan extract. Also, the sample film containing the sappan extract gives an increase yellowness values due to the brazilin present changing in ethanolic solutions to brazilein. The shade of color (ΔE) showed greater values in the films incorporated with the natural colorants because of the polyphenolic compounds found within the natural colorant extract.

The light transmission properties of films was measured by UV-Vis spectroscopy. The detection wavelengths covered the UV and visible light ranges (200 nm to 800 nm). Table 2 and Figure 3 show the transmittance results of the films at different wavelength regions, which are UV-C (280 nm), UV-B (315 nm), UV-A (400 nm), and visible region (700 nm). Pure PLA without natural colorant presented a high light transmission due to PLA possessing a semi-crystalline polymer structure allowing a light transmission of around 97% to 99%. While PLA films mixed with the roselle extract show a decrease in percentage of light transmission at 71% to 91% with 0.1 wt% RS and with further increase in the concentration of roselle extract a further reduction in light transmission to 65% to 91%. The PLA film with sappan extract gave the lowest light transmission of all samples. The %transmission results gave values between 64% to 90% for 0.1 wt% SP and 46% to 90% for 0.2 wt% SP. These results stem from the chemical structures of the natural colorants such as aromatic rings and polyphenol structures. UV-Vis absorption ability of films mixed with roselle and sappan extract is influenced by the electron density in polyphenol compounds which are absorb light at different wavelengths [20,21].

Figure 4 shows the water vapor transmission rate (WVTR) of sample films, which were tested at two time points (7 days and 14 days). The PLA film without natural colorant shows a high-water vapor transmission rate at 4.69 $g{\cdot}m^{-2}$*day. After the PLA film is combined with RS and SP extracts, there is a decrease in WVTR depending on extract concentration. At 0.1 wt% RS and 0.2 wt% RS WVTR values are 4.00 and 4.09 $g{\cdot}m^{-2}$*day respectively. While, at 0.1 wt% SP and 0.2 wt% SP the values are 4.02 and 2.98 $g{\cdot}m^{-2}$*day. These values compared with pure PLA are generally only slightly lower in WVTR value at 7 days with only the 0.2 wt% SP sample giving a larger difference.

Whereas after 14 days, WVTR of all films are lower than the 7 days value. The WVTR of sample films incorporated with extract show a reduction in the hydrophilicity of the films because of the compact network of the polymer chain and color components that generate hydrogen bonding interactions [27,28].

The mechanical properties of the sample films were tested by tensile testing, with the results presented in Figure 5. The graphs are separated into three parts: tensile strength, % elongation and modulus. Each sample is also tested in transverse (TD) and machine directions (MD), these refers to the alignment of the films after being blown into films from the blown film extruder. Tensile strength of pure PLA exhibits a lower tensile strength when compared with films mixed with the natural color extracts. Higher extract concentrations showed slightly higher tensile strength because the natural color extracts (roselle and sappan) contain high polyphenolic contents that leads to hydrogen bonding between the polymer chains [10,29]. % Elongation at break of the films showed the less difference in the transverse direction but in machine direction the % elongation was lower of samples containing extract as compared to the pure PLA film, as the extract can reduce polymer chain mobility. However, PLA with natural colorant showed an improvement in the tensile modulus of the films.

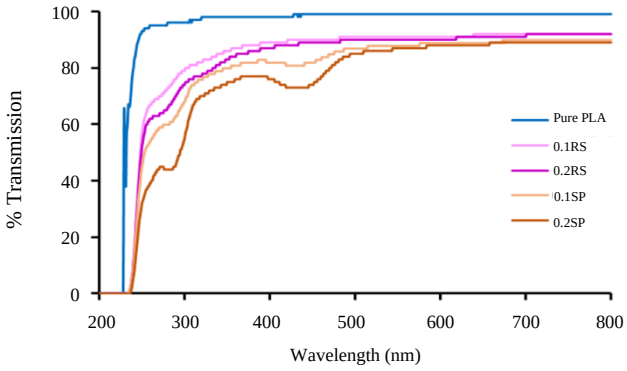

Figure 3. Light transmission spectra of biodegradable films incorporated with roselle and sappan heartwood extraction.

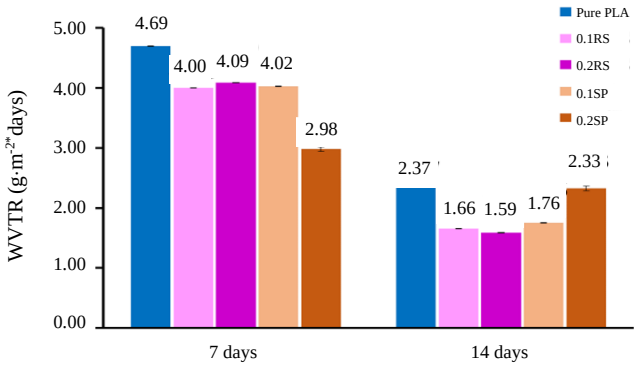

Figure 4. Water vapor transmission rate of biodegradable film incorporated with roselle and sappan extraction.

Table 2. Light transmission of biodegradable films.

	%Transmission			
Sample	**%T at 280 nm (UV-C region)**	**%T at 315 nm (UV-B region)**	**%T at 400 nm (UV-A region)**	**%T at 700 nm (Visible region)**
PLA	97.00 ± 2.64	96.66 ± 2.08	98.66 ± 1.15	99.33 ± 0.57
0.1RS	71.67 ± 1.15	87.67 ± 1.53	88.00 ± 1.00	91.33 ± 1.00
0.2RS	65.67 ± 1.53	76.67 ± 1.53	87.00 ± 1.00	91.00 ± 1.00
0.1SP	64.00 ± 2.65	74.33 ± 4.04	83.67 ± 1.53	90.67 ± 0.58
0.2SP	46.00 ± 2.65	71.33 ± 2.52	78.00 ± 2.00	90.00 ± 1.00

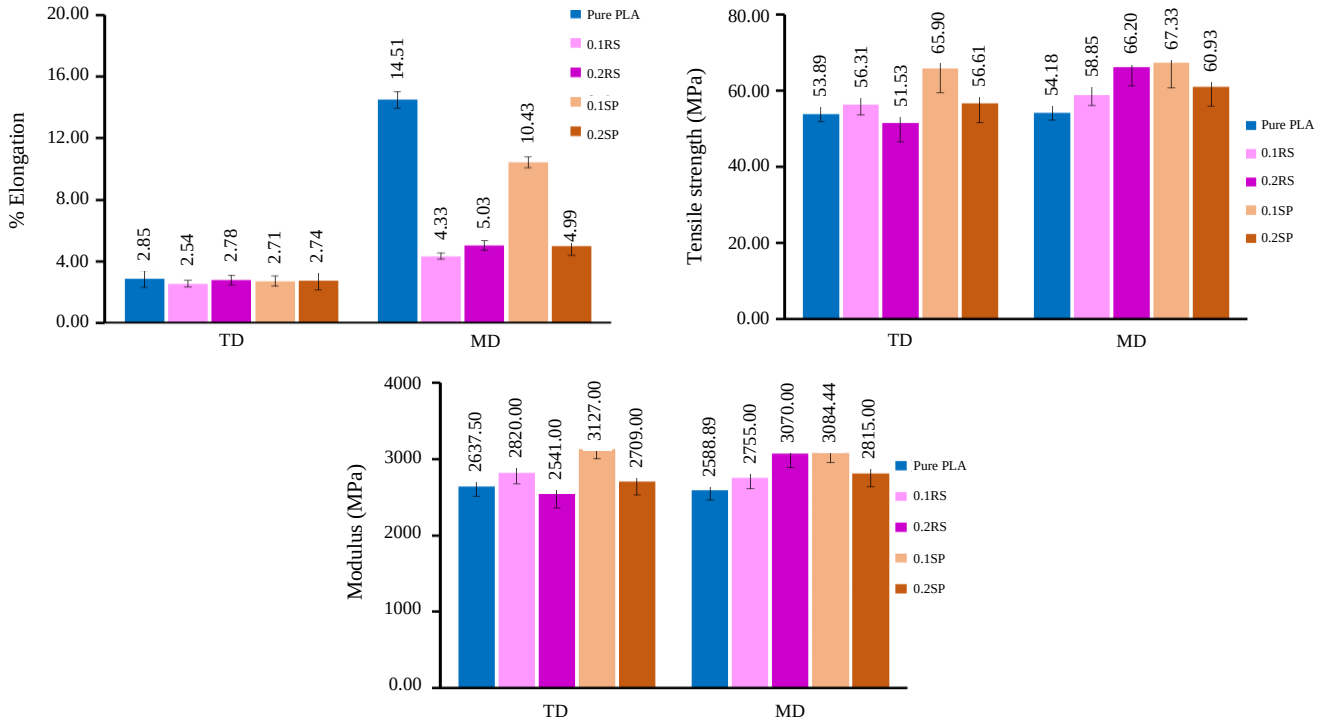

Figure 5. Tensile property of biodegradable films incorporated with roselle and sappapn extraction

X-ray diffraction results of the sample films are presented in in Figure 6. The X-ray diffraction pattern of pure PLA film without roselle and sappan gives rise to a board peak at around 17° and 30°, which is consistent with the standard x-ray pattern of amorphous PLA [30]. Films containing PLA with roselle and sappan extract gave alternate diffraction peaks. The incorporation of natural color extracts into the films produced an increase in the XRD peak intensity at the 17° (2θ). Considering the films mixed with 0.1 wt%, 0.2 wt% roselle and 0.2 wt% of sappan extract gave the highest XRD peak intensities, suggesting that the polyphenol compounds give rise to hydrogen bonding within the film [21,31]. These results are consistent throughout the entire body of work, from WVTR, which found an increase in water vapor barrier properties, DSC thermogram (second heat) improved the T_m and crystallinity and tensile properties, which were slightly increased when the natural colorant extract was incorporated in to the polymer.

DSC thermograms of biodegradable films incorporated with natural colors is presented in Figure 7 for the first heating step and Table 3 for the second heating step. The results in Figure 7 show the first heating cycle of biodegradable film combined with natural colorants, show that the glass transition temperature (T_g) increases slightly when compared with pure PLA due to the steric effect of the bulky structure of colorant molecules with in roselle and sappan extracts. The degree of crystallinity (X_c) of the films containing the extracts is also reduced, which is influenced by the natural color composition. However, the results of the second heating cycle in Table 4 shows there is a slightly increase in glass transition temperature (T_g), and melting temperature (T_m) from the films containing the natural colors. Moreover, the degree of crystallinity increased with higher amounts of the extracts from 28.58% of PLA up to 33.34% for 0.2 wt% RS, 37.57 and 35.51% for 0.1 wt% and 0.2 wt% SP, respectively. This is because of the polymer chain rearrangement and the effect of the polar groups in the natural colors extracts [32].

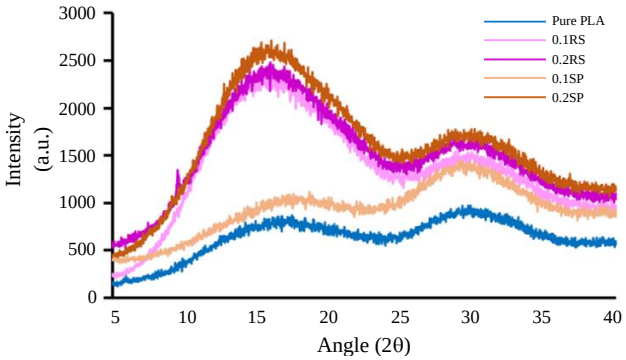

Figure 6. X-ray diffraction pattern of biodegradable films incorporated with roselle calyx and sappan heartwood extraction.

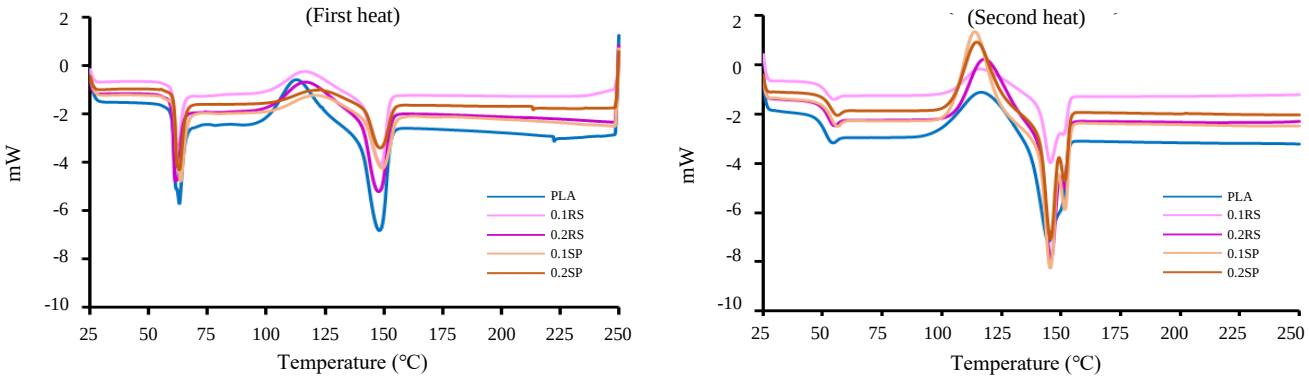

Figure 7. DSC thermogram of biodegradable films incorporated with natural color (First heat) and (second heat).

Table 3. DSC thermogram of biodegradable films incorporated with natural color (Second heat).

Sample	T_g (°C)	T_c (°C)	H_c (J·g^{-1})	T_m (°C)	H_m (J·g^{-1})	%X_c
PLA	47.39	116.46	25.48	144.36	-26.78	28.58
0.1RS	48.21	115.99	20.93	145.33	-21.47	22.91
0.2RS	48.90	117.68	31.70	145.33	-31.24	33.34
0.1SP	49.90	113.88	34.52	145.15	-35.20	37.57
0.2SP	49.76	114.70	34.05	145.20	-33.27	35.51

4. Conclusions

In summary, biodegradable packaging films were produced using environmentally friendly materials, these combined PLA with naturally colored compound extracted from roselle calyx and sappan heartwood. The resultant films found that the natural colorants helped to improve the physical and mechanical properties. Films containing roselle calyx and sappan heartwood extract altered the color when compared to that pure PLA films and also showed good UV-Vis light barrier properties. Tensile properties showed a small improvement to the strength of films when natural colorant was added to the film composition. Roselle calyx and sappan heartwood extracts affected the PLA films by improving the interactions between the polymer chains, these produced films with greater crystallinity and thus a decrease in the WVTR. It is thought that the aromatic and polyphenol structure responable for the natural color of the extract also helps with these greater interactions. Therefore, these biodegradable packaging films can be applied to numerous packaging applications. The films are environmentally friendly, non-toxic to human health and fully biodegrade.

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