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Biodegradable Poly(Lactic acid) Based Food Packaging Incorporated with Antioxidant from Extract of Several Plants

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The demand for smart biodegradable food packaging is increasing due to its capability to preserve food product and maintain food stability. Natural antioxidant food packaging based on poly(lactic acid) (PLA) can be synthesized by addition of certain extract of plant into the polymer matrix. In this study, we develop PLA-based antioxidant food packaging modified with extract of turmeric, mangosteen skin and soursop leaves. The as-obtained film were characterized by several thermal and mechanical assessment, antioxidant assay and applied for packaging of orange fruit. The results showed that the PLA based food packaging incorporated with extract of turmeric, mangosteen skin and soursop leaves have antioxidant activity with IC_{50} of 0.83-2.11 %, 0.24-0.30 %, 1.89-4.33 %, respectively. The peaks from FTIR spectra indicated integration of the antioxidant aromatic compound into the polymer matrix. The tensile strength and percentage of elongation of these films were in the range of 12.5-27.83 MPa and 4.00-11.67 %, respectively. DSC curves and XRD diffractogram of these films revealed that these films were semicrystalline. These films have been proved to be an antioxidant food packaging which retarded the rate of decay of orange fruit.

Keywords: Food packaging, Antioxidant, Poly(lactic acid), Turmeric, Mangosteen skin, Soursop leaves.

INTRODUCTION

The active food packaging have been developed since the last decade, involving the efforts to improve antioxidant and/ or antimicrobial properties of the packaging by incorporating additive components into the matrix of packaging film. The addition of these components was aimed to be controlly released into the food products and improve the properties of the products. According to Silva *et al*. [1], the recent trend showed the increase of the usage of natural antioxidant extracted from parts of plants. Various natural antioxidant from extract of plants have been studied, such as essential oils of cinnamon (*Cinnamomum zeylanicum* L.) [2], oregano (*Origanum vulgare* L.) [3], clove (*Syzygium aromaticum* L.) [4], rosemary (*Rosmarinus officinalis* L.) [5], ginger (*Zingiber officinale* Rosc.) [6] and lemongrass (*Cymbopogon citratus*) [7]. Several original plants from Indonesia such as turmeric (*Curcuma longa* Linn), soursop leaves (*Annona muricata* L.) and mangosteen skin (*Garcinia mangostana* L.) have been known as a source of antioxidant. The previous study revealed that turmeric contain antioxidant in the form of flavonoid and phenolic type compounds [8] curcuminoid such as ar-turmerone, (Z)-γ-atlantone, (E)-γ-atlantone, ar-turmeronol and (Z)-α-atlantone [9]. Soursop leaves contain antioxidant such as tannin, flavonoid, polyphenol, *Annonaceuous acetogenius* and saponin [10], whereas mangosteen skin contain flavonoid, tannin and xanton [11-14].

Commercial food packaging are commonly petrochemical based polymers, such as polyethylene terephthalate, ethylene vinyl alcohol and low density polyethylene, which cannot be degraded easily. Many efforts have been done to improve the degradability of the packaging. One of them is by converting the type of polymers from petrochemical based polymers to the natural polymers, such as edible film from corn starch, cassava starch, rice starch and potato starch [15]. Another effort have been done by developing food packaging based on renewable based polymers such as poly(lactic acid) and polyhydroxy alkanoate. Poly(lactic acid), a renewable polymer, is synthesized by esterification of lactic acid from fermentation of by product agriculture waste such as corn starch or rich flour-substance such as maize, sugar and wheat [16]. Poly(lactic acid) have good heat resistance properties and strength as well as elastic polymer [17].

In this study, we have developed a PLA-based antioxidant food packaging modified with extract of turmeric, mangosteen skin and soursop leaves. The food packaging were then applied to pack orange fruit. After certain storage time, the packaged food are examined for the content of vitamin C.

EXPERIMENTAL

Poly(lactic acid) A-101 (m.w. 80,000 g/mol, density 1.24 g/cm^3) was purchased from Shenzen Esun (China). Chloroform C606-4 HPLC grade, was purchased from Merck. Poly(ethylene glycol) (PEG)-400 was purchased from Merck with average molecular weight 380-420, density 1.13 g/mol. Montmorillonite was obtained from Sigma-Aldrich. Turmeric, soursop and mangosteen were purchased from local market in Bogor and extracted with methanol.

General procedure

Preparation of packaging film: 20 g of Poly(lactic acid) were dissolved in 400 mL chloroform and stirred vigorously for 45 min at 55 °C. Then, 1.2 mL of PEG was added, stirring was continued for 15 min. 1 g of montmorillonite (MMT) was added and stirring was continued for 15 min. 4 mL of extract was added and stirring was continued for 15 min. Solutions were poured onto flat mold. Then, solutions were dried into films at 35 °C for 5 h.

Scanning electron microscopy: Morphological measurement was done using scanning electron microscopy, the sample were cut at 1 × 1 cm. Then, samples were mounted on bevel samples holder and laminated with aurum in a vacuum. SEM pictures were taken by Zeiss scanning electron microscopy (1-5 kV, 10-17 mm width, 500x magnification).

Wide angle X-ray diffraction: Wide angle X-ray diffraction (WAXD) analysis was carried out by XRD-7000, M/s Shimadzu, Japan using a monochromatic and a Cu radiation source (wavelength 1.54 A at 40 kV and 30 mA). $d_{spacing}$ was calculated using Bragg's law equation.

Differential scanning calorimetry (DSC): Glass transition (T_g), crystalllization (T_c) and melting temperature (T_m) of the films have been studied using Perkin-Elmer Diamond DSC. Samples of 3.5 mg were heated from 30 to 400 °C at a rate of 20 °C/min under a constant flow rate of 20 mL/min nitrogen gas purging through the calorimeter.

FTIR: Prior to the measurement, the samples were washed and cut at 1 × 1 cm. The measurement was conducted using FTIR spectrophotometer (Bruker) Diffuse Reflectance mode. Percentage of transmittance was read in the wavenumber range of 4000-500 cm^{-1}.

Mechanical properties: Tensile strength was assayed using texture analyzer according to the standard method of ASTM D882-09 (2009). Briefly, the samples were cut at 130 mm × 25 mm and placed onto the analyzer. The separation between initial grip and test speed was adjusted at 50 mm and 0.8 mm/s, respectively. Tensile strength was calculated by dividing maximum force achieved at assay with initial cross-sectional area of the samples. The assay of percentage of elongation was done with the same steps as that tensile strength. Percentage of elongation was calculated by the equation below.

$$\text{Elongation (\%)} = \frac{\text{Change of maximum length}}{\text{Initial length}} \times 100$$

Antioxidant assay using DPPH method: The samples were cut into very small pieces, weighed at 0.1 g in the test tube and added by 2 mL of methanol. The mixture was vortexed for 3 min and incubated for 3 h. The mixture was then vortexed again for 3 min and pipetted at certain volume to obtain several various concentration. 1 mL of this samples was reacted with 3 mL of DPPH (200 µM in methanol) and measured its absorbance using UV-visible spectrophotometer at wavelength of 517 nm.

$$\text{Inhibition (\%)} = \frac{(\text{Absorbance}_{\text{initial}} - \text{Absorbance}_{\text{final}})}{\text{Absorbance}_{\text{final}}} \times 100$$

% inhibition was plotted as a function of sample concentration, resulting linear curve of Y = aX + b. IC_{50} was calculated as: (50-b)/a.

Application of antioxidant films for packaging of food products: Films obtained at optimum condition were designed as food packaging in certain forms and applied to pack orange fruit. The capability of the food packaging to preserve the foods was examined by assaying the content of vitamin C at certain storage time. Food products packed by commercial plastic served as a control.

RESULTS AND DISCUSSION

The appearance of antioxidant packaging films in this experiment was shown in Fig. 1. The addition of turmeric extract yielded bright yellow film, thus it can improve the appearance of the film and make the packaging more attractive. Brownish dark green and brownish yellow film were resulted from addition of soursop leaves and mangosteen skin, respectively.

FTIR characterization: FTIR spectra (Fig. 2) showed peak at 1800-1700 cm^{-1}, which corresponds to C=O groups of ketone and peak at 1250-1000 cm^{-1} assigned for –CO- alcohol. Small peak at 1500-1400 cm^{-1} related to aromatic C=C. Aliphatic C-H group was shown as peaks at 3000-2850 cm^{-1}. Peak for hydroxyl groups ν(-OH) which was commonly revealed at 3600-3200 cm^{-1}, in this spectra was moderately small and very

Fig. 1. Poly(lactic acid) based films modified with mangosteen skin (a), soursop leaves (b) and turmeric extract (c)

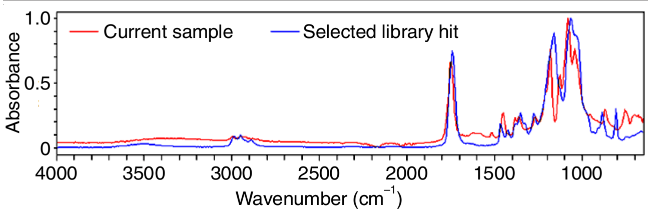

Fig. 2. FTIR spectra of PLA-based films modified with turmeric extract

broad. It may due to the high abundance of these groups and the heterogeneous chemical environment. These hydroxyl groups were from PLA, PEG and antioxidant from extract. Ketone groups were also contributed from PLA and antioxidant from extract.

Antioxidant properties: Fig. 3 showed that PLA-based films modified with mangosteen skin extract have highest antioxidant capacity than that modified with turmeric and soursop leaves, as shown by the lowest IC_{50}. Volume of mixture poured to the mold has no influence to the IC_{50} value for films modified with mangosteen skin. For films containing extract of soursop leaves, increasing volume of mixture from 50 mL to 80 mL significantly reduce the IC_{50}. This may caused by the increase of antioxidant quantity in the film. On the contrary, films containing extract of turmeric showed a decrease in IC_{50} when the volume of mixture was decreased. This pheno-menon may be influenced by the interaction of antioxidant component and polymer molecules which less effective at high volume of mixture, thus the antioxidant may be separated from the matrix of polymers and did not contribute to the overall antioxidant capacity.

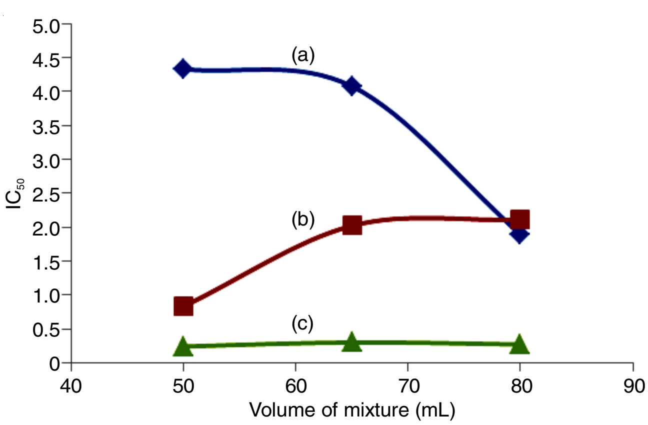

Fig. 3. IC_{50} of PLA-based films modified with soursop leaves (a), turmeric (b) and mangosteen skin extract (c) at various volume of mixture

Mechanical properties: Mechanical strength of PLA-based films modified with turmeric extract was significantly influenced by volume of mixture poured to the mold. The higher the volume of mixture, or the thicker the films, the lower the tensile strength. This may be due to the films that was harder and more brittle as the thickness of the films was increasing, thus the flexibility and elasticity decreases. Li and Huneault [18] explained that adhesion power between interface of polymer phases greatly influenced the tensile strength. The decrease of tensile strength was due to the lowering of adhesion power between interface of polymer phases.

Table-1 showed that for PLA-based films modified with turmeric extract, the higher the volume of mixture, the lower the tensile strength and the higher the percentage of elongation, indicated the less flexible of the films. This may due to the fact that the greater the thickness of the films, the higher the crystallinity of the films. The crystallinity of the films can be confirmed by DSC and XRD.

TABLE-1
MECHANICAL PROPERTIES OF PLA BASED FILMS MODIFIED WITH TURMERIC EXTRACT

Volume of mixture poured to the mold (mL)	Tensile strength (kgf/cm^2)	Average tensile strength (kgf/cm^2)	Average tensile strength (MPa)	Elongation (%)
80	125.08 129.94 127.40	127.47	12.50	11.67
65	154.70 156.75 156.38	155.94	15.29	5.33
50	282.39 231.45 282.39	265.41	26.03	4.00

Poly(lactic acid)-based films modified with soursop leaves extract showed reverse trend (Table-2). The higher the volume of mixture, the higher the tensile strength and the lower the percentage of elongation. This indicated the increase in film thickness was still allowed effective interaction between polymer molecules. From the trend of the tensile strength, the percentage of elongation can be predicted and the result matched with the prediction. Similar results were obtained for PLA- based films modified with mangosteen skin, though for volume of 65 mL the tensile strength was not significantly different from that of volume of 80 mL (Table-3). Most of the tensile strength obtained for these films in the experiment were above 20 MPa, similar as that of commercial plastic. Many commercial bioplastics such as Biobag, Eco Film™ dan Eco Works™ have tensile strength in the range of 13-21 MPa [19].

DSC characterization: DSC curves of PLA-based films modified with extracts showed peaks for both T_g and T_m, indicated that the films were semicrystalline. Table-4 showed a decrease in T_g at increasing of volume from 65 to 80 mL. This phenomenon may be due to an increase in the mobility of polymer chain [20]. This result was in agreement with mecha-nical properties assay which confirmed that the tensile strength at volume of 80 mL was lower than that at volume of 65 mL.

TABLE-2
MECHANICAL PROPERTIES OF PLA BASED FILMS MODIFIED WITH SOURSOP LEAVES EXTRACT

Volume of mixture poured to the mold (mL)	Tensile strength (kgf/cm^2)	Average tensile strength (kgf/cm^2)	Average tensile strength (MPa)	Elongation (%)
80	275.10 276.50 281.67	277.76	27.24	6.33
65	244.20 244.77 241.67	243.55	23.88	7.00
50	203.85 203.39 205.36	204.20	20.03	8.00

TABLE-3
MECHANICAL PROPERTIES OF PLA BASED FILMS MODIFIED WITH MANGOSTEEN SKIN EXTRACT

Volume of mixture poured to the mold (mL)	Tensile strength (kgf/cm^2)	Average tensile strength (kgf/cm^2)	Average tensile strength (MPa)	Elongation (%)
80	285.95 287.50 277.78	283.74	27.83	4.33
65	279.80 281.77 283.04	281.54	27.61	7.33
50	259.18 259.68 266.92	261.93	25.69	8.00

Both T_m and T_c values of PLA-based films modified with turmeric extract were similar at various volume of mixture, *i.e.* 66-69 °C and 139-140 °C, respectively. These T_m values were lower than that of PLA-based films modified with mangosteen skin extract, indicated the lower crystallinity and the higher mobility of polymer chain. Thus, the tensile strength of PLA-based films modified with turmeric extract were relatively lower than that of PLA-based films modified with mangosteen skin extract.

XRD characterization: XRD diffractogram revealed small, broad peaks, indicated the films were all semicrystalline. The result was in agreement with that obtained from DSC curves. The values of 2θ and d-spacing from XRD peaks were listed in Table-5. At small angle area of 2θ below 10°, there were an intense peak at about 5°, corresponds to montmorillonite. These peaks may shift to smaller value due to interaction of MMT with polymers and antioxidant, which creates wider interlayer of MMT. Poly(lactic acid) peaks were shown at 2θ of 14.7-14.9°, 16.6-16.7°, 19.7-19.8° and 24.8-24.9°. This values were similar to the result obtained by Lin and Huneault [18] who reported neat PLA peaks at of 2θ of 15.04, 16.94, 19.25 and 22.60°, related to crystalline structure in the form of a. The shifts were due to the interaction between PLA and other components.

SEM characterization: SEM image has high capability to provide information about morphological properties of film surface and homogeneity of the distribution of additive component onto polymer matrix. Inhomogeneous of distribution of antioxidant in the packaging film resulted less effectiveness in preserving the packed food products. SEM image of PLA-based films modified with turmeric, soursop leaves and mangosteen skin extract (Fig. 4) showed no phase separation between polymer matrix and other components and homogeneous distribution of components in the polymer matrix.

Application of PLA-based films modified with extracts as food packaging: The films obtained at optimum condition in the experiment was folded and sealed to form a packaging and was then applied as food packaging for orange fruit. The selection of this kind of food product is based on the high vitamin C content, thus represented the food product which contain vitamin C as main component.

Fig. 5 showed that decrease of vitamin C in orange fruit packed with PLA-based films modified with turmeric, soursop leaves and mangosteen skin extract were lower than that of control. At storage time of two days, vitamin C content in orange fruit packed with PLA-based films modified with turmeric and mangosteen skin extract was hardly changed, whereas at the same storage time, the PLA-based films modified with soursop leaves showed a significant decrease in vitamin C content. However, compared to the control, the percentage of decrease was lower for PLA-based films. It means that these PLA-based films have great contribution in oxygen scavenging and inhibition of vitamin C oxidation. The decrease of vitamin C in orange fruit

TABLE-4
T_g, T_m, T_c, ΔH_m, ΔH_c VALUES FOR PLA BASED FILMS MODIFIED WITH TURMERIC, SOURSOP LEAVES AND MANGOSTEEN SKIN EXTRACT

Extract	Volume (mL)	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (mcal)	ΔH_m (J/g)	ΔH_c (mcal)	ΔH_c (J/g)	ΔH_m - ΔH_c (J/g)
Turmeric	50	–	69.57	140.43	8.08	11.31	-11.41	-15.97	4.66
	65	50	66.83	139.29	7.66	10.72	-10.87	-15.22	4.50
	80	45	68.24	140.43	7.71	10.79	-10.85	-15.19	4.40
Mangos-teen skin	50	53	84.41	143.02	10.34	14.48	-9.27	-12.98	1.50
	65	55	79.49	141.65	11.08	15.51	-9.94	-13.92	1.59
	80	–	80.73	139.84	5.32	7.45	-7.58	-10.61	3.16
Soursop leaves	50	59	85.01	143.12	11.76	16.46	-7.13	-9.98	6.48
	65	58	84.70	141.88	10.23	14.32	-6.09	-8.53	5.79
	80	–	72.38	140.48	3.83	5.36	-8.88	-12.43	7.07

TABLE-5
VALUES OF 2θ AND d-SPACING FROM XRD PEAKS FOR PLA BASED FILMS MODIFIED WITH TURMERIC, SOURSOP LEAVES AND MANGOSTEEN SKIN EXTRACT

2θ (turmeric)	d-spacing (turmeric)	2θ (soursop leaves)	d-spacing (soursop leaves)	2θ (mangosteen skin)	d-spacing (mangosteen skin)	Component
5.0702	17.42953	5.3822	16.41984	5.0702	17.42953	MMT
9.8397	8.98926	9.9243	8.91285	9.9350	8.90326	MMT
14.7861	5.99134	14.8954	5.94764	14.9323	5.93299	PLA
16.6223	5.33342	16.7628	5.28901	16.7186	5.30290	PLA
19.8785	4.46650	19.8594	4.47075	19.7322	4.49928	PLA
24.9323	3.57142	24.9187	3.57334	24.8990	3.57612	PLA

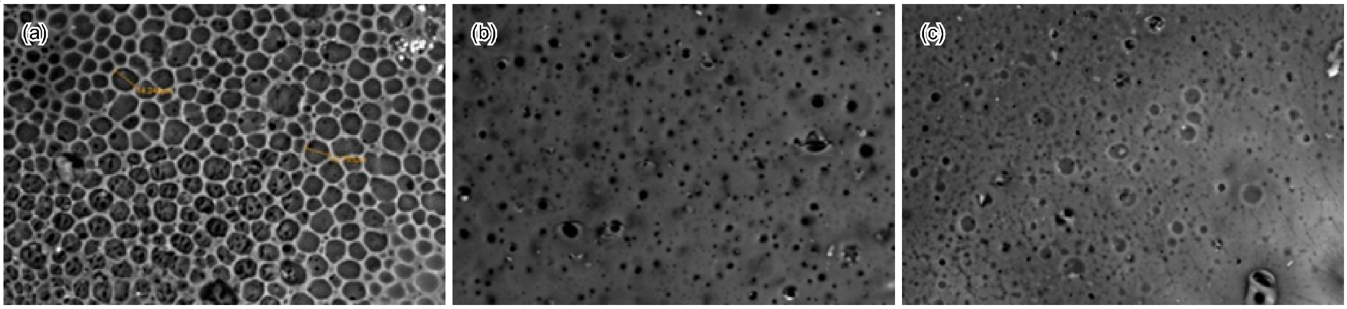

Fig. 4. SEM images of PLA based films modified with turmeric (a), soursop leaves (b) and mangosteen skin (c) extract

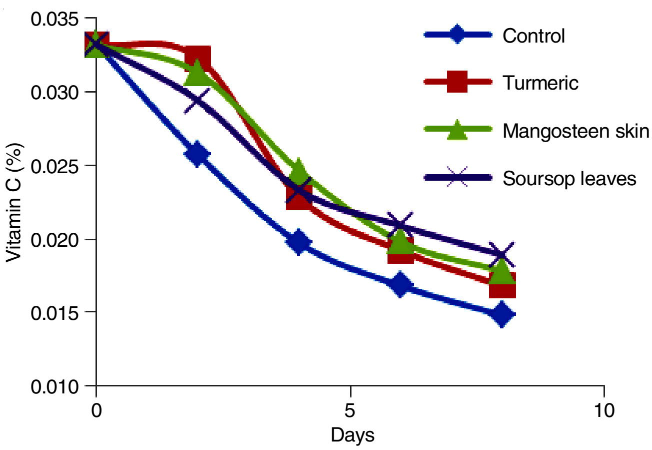

Fig. 5. Vitamin C content (%) in orange fruit packed with PLA-based films modified with turmeric, soursop leaves and mangosteen skin extract

for control was going on from initial day until 8 days, indicated that the packaging cannot preserve the quality of packed food product.

Conclusion

Poly(lactic acid)-based food packaging incorporated with extract of turmeric, mangosteen skin and soursop leaves have antioxidant activity with IC_{50} in the range of 0.83-2.11 %, 0.24-0.30 %, 1.89-4.33 %, respectively. The FTIR spectra revealed peaks for –OH and C=O ketone, -C-O alcohol and aromatic C=C, indicating the integration of the antioxidant aromatic compound into the polymer matrix. The tensile strength and percentage of elongation of these films were in the range of 12.5-27.83 MPa and 4.00-11.67 %, respectively. The IC_{50} value and mechanical properties depends on the volume of mixture poured to the mold. DSC curves and XRD diffractogram of these films revealed that these films were semi-crystalline, with the degree of crystallinity depends on the volume of mixture. These films have been proved to be an antioxidant food packaging which retarded the rate of decay of several kinds of food product.

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