The 4th International Conference on Agriculture and Agro-Industry
ICAAI2022
Transforming Value Chains for Global Security
Mae Fah Luang University, Chiang Rai, Thailand
November 10 -11, 2022

Journal of Food Science and Agricultural Technology

International peer-reviewed scientific online journal Published online: http://rs.mfu.ac.th/ojs/index.php/jfat

Original Research Article

Preparation and Characterization of Biodegradable Thermoformed Tray from Thermoplastic Cassava Starch/poly(lactic acid) Blend Incorporating Encapsulated Black Pepper Essential Oil

Chanakorn Yokesahachart[1], Jaruporn Rakmai[2], Udomluk Sukatta[2], Prapassorn Rugthaworn[2], Keowpetch Lobyam[2], and Nattaporn Khanoonkon[2*]

[1] Department of Food Science and Technology, Faculty of Agricultural Technology and Agro-Industry, Rajamangala University of Technology Suvarnabhumi, Phra Nakhon Si Ayutthaya 13000, Thailand
[2] Kasetsart Agricultural and Agro-Industrial Product Improvement Institute, Kasetsart University, Bangkok 10900, Thailand

ARTICLE INFO

Article history:
Received 7 September 2022
Received in revised form 3 October 2022
Accepted 10 November 2022
Published 6 December 2022

Keywords:
Black pepper essential oil
Encapsulation
Poly(lactic acid)
Thermoplastic cassava starch
Thermoforming trays

ABSTRACT

This current research aims to study the preparation and characterization of thermoformed trays from poly(lactic acid)/thermoplastic cassava starch (PLA/TPS) and PLA/TPS incorporating encapsulated black pepper essential oil. The weight ratio of PLA: TPS was fixed at 60:40. The black pepper essential oil (BP) was encapsulated in hydroxypropyl-beta-cyclodextrin (HPBCD) and maltodextrin-gum arabic (MG) using spray-drying technique. The BP-HPBCD and BP-MG varied as 10%, 15%, and 20% w/w. PLA/TPS, PLA/TPS/BP-HPBCD, and PLA/TPS/BP-MG thermoformed trays were successfully prepared by using thermoforming machine with a heating temperature of 340 °C, a heating time of 30 s, a vacuum time of 15 s and a cooling time of 15 s. PLA/TPS and PLA/TPS/BP-HPBCD thermoformed trays were pale yellow, whereas PLA/TPS/BP-MG thermoformed trays were yellow. Trays from PLA/TPS/BP-MG were easier to form in complete shape than those from PLA/TPS/BP-HPBCD using thermoforming machine. The loss percentage of active compounds in BP of PLA/TPS/BP-MG and PLA/TPS/BP-HPBCD thermoformed trays were determined by Gas Chromatography-Mass Spectrometry (GC-MS). The lowest loss of active compounds in BP were beta-caryophyllene and d-limonene, which lost in thermoforming step from PLA/TPS/BP-MG about 93.30-96.90% and 89.05-89.93%, respectively. Both thermoformed trays from PLA/TPS/BP-HPBCD and PLA/TPS/BP-MG tended to decompose when buried in the soil condition. PLA/TPS/BP-HPBCD and PLA/TPS/BP-MG have been potentially prepared and converted to biodegradable thermoformed trays.

* *Corresponding author.* Tel.: 02-9428600
E-mail address: E-mail: aapnok@ku.ac.th

ISSN: 2408-1736

INTRODUCTION

During the environmental concerns as well as COVID-19 pandemics, the growth of environmentally friendly packaging became more interesting. The study of biodegradability of packaging became a significant issue in Thailand. The utilization of biodegradable materials, i.e., poly(lactic acid) (PLA), and thermoplastic starch (TPS) for packaging application were more pronounced (Amin et al., 2022). For the food packaging application, the potential of packaging to prolong the shelf life of food is the most significant (Ahmed et al., 2022). The active antimicrobial and antioxidant properties of the packaging had been reported to extent the shelf life of many kinds of food products, i.e., meat (Song et al., 2020), bread (Viscusi et al., 2021), etc.

Natural essential oils i.e., cinnamon (Simionato et al., 2019), thymol (Celebioglu et al., 2018), green tea (Song et al., 2020), rosemary (Song et al., 2020), black pepper (Rakmai et al., 2017; Rakmai et al., 2022), etc had been reported as active compound for antimicrobial and antioxidant packaging. However, these oils were lost when utilized at high temperatures resulting in loss of active properties (Woranuch, et al., 2013). The encapsulation technique was used to protect the loss of essential substances (Celebioglu et al., 2018; Karaaslan et al., 2021 Rakmai et al., 2017; Rakmai et al., 2022; Woranuch, et al., 2013). Many researches had been reported that the thermal stability of essential oils increased when encapsulated in wall materials, i.e., hydroxypropyl-beta-cyclodextrin (HPBCD) (Celebioglu et al., 2018), maltodextrin-gum arabic (MG) (Karaaslan et al., 2021), etc. However, the effect of the encapsulated essential oils after passing the 3-steps of high thermal conventional converting process on their processibility as well as loss of active compound contents was less explained.

Therefore, this research aims to study the effects of encapsulated BP essential oils with different wall materials, i.e., HPBCD and MG) on processibility 3-steps of processing; i) extrusion, ii) sheet extrusion and thermoforming of PLA/TPS blend. The loss active compound contents of the PLA/TPS blends in each process and the soil burial property of the blend were investigated.

MATERIALS AND METHODS

Materials

Black pepper essential oil (BP) was purchased from Botanicessence (Bangkok, Thailand), which has 97% purity, boiling point of 84 °C and flash point of 189 °C. Hydroxypropyl-beta-cyclodextrin (HPBCD) was obtained from Chanjao Longevity Co., Ltd. (Bangkok, Thailand). Arabic gum and maltodextrin were purchased from Krungthepchemi Co., Ltd. (Bangkok, Thailand). Muller-Hinton Broth (MHB) and Muller-Hinton Agar were purchased from Merck (Darmstadt, Germany). Cassava starch was supplied by Tongchan Co., Ltd. (Bangkok, Thailand). PLA (Ingeo™ 2003D) was obtained from Nature Works LLC (Minnesota, USA), which had a melting temperature in the range of 145-160 °C and melt flow ability of 6 g/10 min. Glycerol used was a commercial grade product. All other chemicals/reagents used for analysis were analytical grade.

Preparation of poly(lactic acid)/thermoplastic starch/black pepper encapsulated blend resins, sheets, and thermoforming trays

Cassava starch was mixed with glycerol plasticizer at contents of 35 parts per hundred parts of starch and fed into a twin-screw extruder (LTE-26-40, Labtech Engineering Co., Ltd., Thailand, L/D = 40). The temperature profile along the extruder barrel was set in a range from 80 °C to 155 °C. The extrudates were cut by a pelletizer (LZ-120, Labtech Engineering Co., Ltd., Thailand) to obtain 2.5-mm length pellets. The TPS pellets were dried at 50 °C overnight and kept in desiccators containing silica gel at an ambient temperature.

PLA/TPS blends incorporating BP encapsulates were prepared by mixing a fixed weight ratio of PLA:TPS of 60:40 and encapsulated BP. The contents of encapsulated BP, i.e. BP-HPBCD and BP-MG (maximum of both MICs and MBCs against four strains of meat spoilage bacteria, i.e., *Escherichia coli*, *Micrococcus luteus*, *Salmonella Typhimurium*, and *Staphylococcus aureus* = 102,400 mg/mL), varied from 10%, 15%, and 20%. The PLA/TPS pellets were physically mixed with encapsulated material and subsequently fed into the twin-screw extruder. The extrusion was done using a temperature range of 70-155 °C and a screw speed of 150 rpm and pelletized to obtain 2.5-mm length pellets. The PLA/TPS/encapsulated BP pellets were dried at 50 °C overnight and kept in desiccators containing silica gel at an ambient temperature before the test.

The obtained PLA/TPS/encapsulated BP samples were dried at 50 °C for 24 h in a hot-air oven before conversion into sheets by using a single-screw sheet extrusion (SE-D30L30, CHAREON TUT CO., LTD., Thailand) connected with a Cast film/sheet line (CF-W400, CHAREON TUT CO., LTD., Thailand). The sheet extrusion was performed using barrel temperature in the range of 120-165 °C, screw speed in the range of 35-47 rpm and the calendering roll speed range of 1.0-2.4 rpm. The thickness of the sheets was controlled in the range of 0.4-0.5 mm.

The packaging trays of PLA/TPS/encapsulated BP were performed using a thermoforming machine (EMV200, ENMACH CO., LTD., Thailand). The obtained sheet was cut into square shape with an area of 25×25 cm^2, then formed to be thermoformed trays using a heating temperature of 340 °C, heating time of 30-50 s, vacuum time of 15 s and cooling time of 15-30 s.

Determination of polylactic acid/thermoplastic starch/black pepper encapsulated blend resin, sheet, and thermoforming tray loss active compound contents

The analyses were performed on a gas chromatography-mass spectrometry (GC-MS) QP2020 NX (Shimadzu) equipped with a headspace sampler HS-20 (Shimadzu). The fused silica capillary column (30 m × 0.25 mm i.d., coated with TRB 5 MS, 0.25 μm film thickness) was used. The injector and interface operated at 250 °C and 300 °C, respectively. Column temperature was programmed to rise from 50 °C to 290°C at a heating rate of 4 °C/min. The carrier gas was helium with a flow of 1.0 mL/min. 500 μL samples were injected (splitless) for HS. Conditions for post run were set as back flush for 1.89 min, at 280 °C, with helium at 50 psi. MS conditions were as follows: ionization voltage of 70 eV, acquisition mass range 50-650, scan time 0.32 s. Chemical compositions were identified by comparison of their linear retention indexes to MS data library. The remaining beta-caryophyllene and d-limonene was determined to represent BP as followed Eq. (1):

$$Area_{bp}/Area_{ec} \times 100 \quad (1)$$

Where $Area_{bp}$ is peak area of active compound in bioplastic (PLA/TPS blend), $Area_{ec}$ is peak area of active compound in encapsulated wall material (HPBCD or MG).

Soil burial biodegradable test of polylactic acid/thermoplastic starch/black pepper encapsulated blend trays

The biodegradation of PLA/TPS /encapsulated BP thermoformed tray was studied under outdoor soil conditions for 1 month (during April 19th,2021 to May 19th, 2021) at Rajamangala University of Technology Suvarnabhumi, Phra Nakhon Si Ayutthaya Province, Thailand. The specimens were buried in the soil at a depth of approximately 30 cm. The average atmosphere temperature was 30-32 °C and 80% of RH.

RESULTS AND DISCUSSION

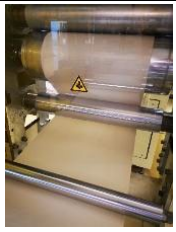
Appearances and processibility of PLA/TPS/black pepper encapsulation trays

The appearance of PLA/TPS blend resin after extrusion process was opaque white, whereas the blend incorporating encapsulated BP was opaque yellow (Table 1). The BP-HPBCD was less affected by the yellowness of the blends than the BP-MG. The yellowness of the blends was more pronounced when the encapsulated BP content increased due to the high number of degraded encapsulated materials. All samples of resin could be prepared using the same temperature and screw speed, indicating that no effect of encapsulated BP on the processibility of the extrusion resins.

By considering the PLA/TPS and PLA/TPS/encapsulated BP sheet samples, all samples could be prepared by the sheet extrusion process. PLA/TPS sheet exhibited opaque white with smooth surface, while the PLA/TPS/BP-HPBCD samples were rougher surfaces with pale yellow. The sheet extrusion processibility of PLA/TPS/BP-HPBCD became poor, and the surface roughness of sheet became more pronounced when BP-HPBCD content was increased, suggesting incompatibility and phase separation. Similar to the result from Wang et al. (2017), they developed antimicrobial PLA film using allyl isothiocyanate encapsulated in beta-cyclodextrin (BCD) as an active compound. The result showed that the suitable content of allyl isothiocyanate-BCD encapsulate was 10% w/w with promoted extensibility of the film due to plasticizing effect. However, increasing encapsulate content to 15-20 % w/w caused phase separation of the film. In contrast, the processibility of PLA/TPS containing BP-MG sheets were better when compared with those containing BP-HPBCD. The sheet surfaces of PLA/TPS/BP-MG were smoother through the 20% w/w of BP-MG. This evidence confirmed that the BP-MG was less affected by processability and PLA/TPS sheet surface than BP-HPBCD.

The PLA/TPS tray samples were successfully prepared by thermoforming process, while PLA/TPS trays containing 15-20% of BP-HPBCD could not be formed in complete shape due to phase separation. However, all active PLA/TPS/BP-MG packaging trays were successfully prepared. The result suggested that the encapsulated wall materials significantly affected on thermoforming processibility of the trays. Moreover, the brittleness of trays became more pronounced when increasing BP-MG content.

Table 1. Appearances of PLA/TPS and PLA/TPS/black pepper encapsulates after extrusion, sheet extrusion, and thermoforming process.

sample	Appearances		
	Resins	Sheets	Thermoforming Trays
PLA/TPS			
PLA/TPS/BP-HPBCD10			
PLA/TPS/BP-HPBCD15			No sample
PLA/TPS/BP-HPBCD20			No sample

sample	Appearances		
	Resins	Sheets	Thermoforming Trays
PLA/TPS/BP-MG10			
PLA/TPS/BP-MG15			
PLA/TPS/BP-MG20			

Table 2. Loss percentage of active compounds of encapsulated BP in HPBCD and MG wall materials after extrusion, sheet extrusion, and thermoforming process.

Sample	Active compound types	Initial load contents (g/100g)	Loss percentage of active compounds (%) (Converting process)		
			Resins (Extrusion)	Sheets (Sheet extrusion)	Trays (Thermoforming)
PLA/TPS/BP-HPBCD10	limonene caryophyllene	10.00	90.90 99.40	98.00 ND	98.30 ND
PLA/TPS/BP-HPBCD15	limonene caryophyllene	15.00	75.87 -	91.53 -	No sample
PLA/TPS/BP-HPBCD20	limonene caryophyllene	20.00	67.15 -	82.15 -	No sample
PLA/TPS/BP-MG10	limonene caryophyllene	10.00	61.50 89.50	86.50 96.50	89.40 96.90
PLA/TPS/BP-MG15	limonene caryophyllene	15.00	73.53 79.80	89.27 93.93	89.93 95.53
PLA/TPS/BP-MG20	limonene caryophyllene	20.00	33.30 70.90	80.75 84.60	89.05 93.30

Loss percentage of active compounds of encapsulated BP in HPBCD and MG wall materials after extrusion, sheet extrusion, and thermoforming process

In this research, encapsulated BP was incorporated in PLA/TPS blends and formed into packaging tray by using 3 steps of converting: i) extrusion process at the temperature range of 80-155 °C, ii) sheet extrusion at the temperature range of 120-165 °C, and iii) thermoforming at the temperature of 340 °C with 30-50 s of heating time. The BP-HPBDC and BP-MG encapsulated with contents of 10, 15 and 20 parts per hundred parts of PLA/TPS blends were used. After the first heating steps, the loss percentage of main active compounds (i.e., beta-caryophyllene and d-limonene) (Bastos et al., 2020) in BP of all trays were enhanced due to evaporation of active compounds. The lowest loss percentage of beta-caryophyllene and d-limonene were found in a PLA/TPS/BP-MG20 sample due to high initial contents of BP and the good protection of MG wall materials. The BP-MG encapsulate was pronounced more thermal stability of BP in PLA/TPS blends than that of BP-HPBDC. The loss percentage of active compounds clearly increased after passing the sheet extrusion and thermoforming due to thermal degradation. However, the loss percentage of active compounds happened more at the first extrusion step due to direct heating of encapsulated materials with barrel and screws of extrusion.

Biodegradation

Figure 1 shows the pictures of the biodegradability of PLA/TPS and PLA/TPS/black pepper encapsulated samples before and after soil burial biodegradable test. The original sample surfaces were relatively smooth without visible cracks before the test. After 30 days of the test, all tray samples were rough surfaces with cracks due to disintegration by hydrolysis. The result confirmed that the addition of BP-HPBCD and BP-MG did not influence the degradation of the blends. However, 30 days of soil burial could not complete the

biodegradation of PLA/TPS in real conditions and should have taken more time. For the mechanism of biodegradability in the soil condition, Lv et al. (2017) explained that the degradation of PLA/TPS blend was heterogeneous degradation, the PLA component in the blend preferred to hydrolyze at the core of the materials, while starch components in the blends preferred to degradation from the surface of blends to the inner of blends.

Figure 1. Appearances before (left) and after (right) soil burial biodegradation of (a) PLAPLA/TPS and (b)-(e) PLA/TPS/black pepper encapsulation; (b) PLA/TPS/BP-HPBCD10, (c) PLA/TPS/BP-MG10, (d) PLA/TPS/BP-MG15, and (e) PLA/TPS/BP-MG20.

CONCLUSIONS

The encapsulates, i.e., BP-HPBCD and BP-MG did not influence on resin extrusion and sheet extrusion processibility of the PLA/TPS blends. However, the addition of BP-HPBCD encapsulates inhibited thermoforming processibility of the blend due to phase separation at content up to 10%. The remaining contents of active compound in BP were highest remaining or lowest loss in PLA/TPS/BP-MG20 sample. The loss of active compounds was highest during the first extrusion step. The biodegradability of PLA/TPS in soil burial did not influence by the addition of BP encapsulates.

ACKNOWLEDGMENTS

The authors would like to thank The National Science and Technology Development Agency (NSTDA) for financial support (Grant No. P-18-51777).

REFERENCES

Ahme, Md.W. Haque, Md.A., Mohibbullah, Md. Khan, Md.S.I., Islam, M.A., Mondal, Md.H.T. and Ahmmed, R. 2022. A review on active packaging for quality and safety of foods: Current trends, applications, prospects and challenges. Food Packaging and Shelf Life, 33, 200913.

Amin, U., Khan, M.K.I., Maan, A.A., Nazir, A., Riaz, S., Khan, M.U., Sultan, M., Munekata, P.E.S. and Lorenzo, J.M. 2022. Biodegradable active, intelligent, and smart packaging materials for food applications. Food Packaging and Shelf Life, 33, 200903.

Bastos, L.P.H., Santos, C.H.C, Carvalho, M.G., and Garcia-Rojas, E.E., 2020. Encapsulation of the black pepper (Piper nigrum L.) essential oil by lactoferrin-sodium alginate complex coacervates: Structural characterization and simulated gastrointestinal conditions. Food Chemistry, 316, 126345.

Celebioglu, A., Yildiz, Z.I. and Uyar, T. 2018. Thymol/cyclodextrin inclusion complex nanofibrous webs: Enhanced water solubility, high thermal stability and antioxidant property of thymol. Food Research International, 106, 280-290.

Karaaslan M., Şengün, F., Cansu, Ü., Başyiğit, B., Sağlam, H. and Karaaslan, A. 2021. Gum arabic/maltodextrin microencapsulation confers peroxidation stability and antimicrobial ability to pepper seed oil. Food Chemistry, 337, 127748.

Lv, S., Zhang, Y., Gu, J., and Tan, H. 2017. Biodegradation behavior and modelling of soil burial effect on degradation rate of PLA blended with starch and wood flour. Colloids and Surfaces B: Colloids and Surfaces B: Biointerfaces, 159, 800–808.

Rakmai, J., Cheirsilp, B., Mejuto, J.C., Torrado-Agrasar, A. and Simal-Gandara, J. 2017. Physico-chemical characterization and evaluation of bio-efficacies of black pepper essential oil encapsulated in hydroxypropyl-beta-cyclodextrin. Food Hydrocolloids, 65, 157-164.

Rakmai, J., Sukatta, U., Rugthaworn, P., Yokesahachart, C., Lobyam,K., and Khanoonkon, N. 2022. Encapsulation of Black Pepper Essential Oil in Maltodextrin-Arabic Gum Mixed Shell and Antimicrobial Activity Evaluation. In proceedings of International Conference on Food and Applied Bioscience (FAB 2022) (pp. 100-107). Information Technology Service Center, Chiang Mai University, Chiang Mai, Thailand.

Song, X.C., Canellas, E., Wrona, M., Becerril, R. and Nerin, C. 2020. Comparison of two antioxidant packaging based on rosemary oleoresin and green tea extract coated on polyethylene terephthalate for extending the shelf life of minced pork meat. Food Packaging and Shelf Life, 26, 100588.

Viscusi, G., Bugatti, V., Vittoria, V., and Gorrasi, G. 2021. Antimicrobial sorbate anchored to layered double hydroxide (LDH) nano-carrier employed as active coating on Polypropylene (PP) packaging: Application to bread stored at ambient temperature. Future Foods, 4, 100063.

Wang J., Qiu, C., Narsimhan, G. and Jin, Z. 2017. Preparation and characterization of ternary antimicrobial films of beta-cyclodextrin/allyl isothiocyanate/polylactic acid for the enhancement of long-term controlled release. Materials,10,1210.

Woranuch, S., Yoksan, R., and Akashi, M. 2013. Ferulic acid-coupled chitosan: Thermal stability and utilization as an antioxidant for biodegradable active packaging film. Carbohydrate Polymers, 115, 744-751.