Evaluation of Heavy Metals and Hazardous Substances in Polylactic Acid for Agricultural Applications

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Abstract

The analysis of the content of heavy metals and hazardous substances in polylactic acid (PLA) biodegradable plastics is an approach to assess for agricultural applications such as plastic mulch. Most plastic mulch products are produced from polyethylene plastic (Polyethylene; PE) that decomposes slowly and causes environmental problems. According to the PLA study that has been tested according to the requirements of the ISO 17088: 2012 standard, the disintegration test between the complete fermentation according to ISO 16929: 2013 (100 percent) and the assessment of the impact of compost on plants according to OECD 208 together with EN 13432 Annex E, the test results reveal that the compost obtained from disintegration test during fermentation does not negatively affect the ability of the compost to plants grow. The results of PLA analysis using the Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) find selenium for 0.05, zinc for 0.43 lead for 0.12, cadmium for less than 0.20, nickel less than for 0.50, chromium for less than 0.50 and copper for less than 0.50 milligrams per kilogram. And selenium, nickel, chromium, and copper found provide the same amount as those found in PE. The results of the analysis for the content of heavy metals and harmful residues in the planting areas of Ratchaburi and Pathum Thani provinces, reveal that there are selenium, zinc, lead, nickel, chromium, copper accumulated in the soil at a quantity about 6-600 times higher than those in PLA, but not exceeding the standard criteria of soil quality used for housing and agriculture. Therefore, it is possible to utilize PLA to produce plastic film covering the soil for environmental friendliness.

Keywords: heavy metals and hazardous substances, Poly Lactic acid, biodegradable plastics

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Introduction

Biodegradable plastic has a tendency to be applied more as agricultural materials such as biodegradable plastic mulch because after harvesting the products, the plowing can be carried on together with the soil preparation for planting in the next round and it does not affect, in the level of toxic residues on the soil and does not cause environmental problems like using the current plastic film for covering the ground which is mainly produced from polyethylene (Polyethylene; PE) that is difficult to disintegrate and cause environmental problems. Biodegradable plastics, therefore, are an alternative material to replace difficult-to-decompose plastics, such as polymers in the polyester group including polylactic acid (PLA), polybutylene succinate (PBS), polybutylene adipate terephthalate:(PBAT) and polycarbonate (PCL), etc. Polyethylene is a widely used plastic and can be improved to have properties suitable for further utilization such as flexibility, resistance to penetrating and tearing, resistance to chemicals and solvents, electrical insulation. Examples of products produced from PE plastics such as shrink films, packaging films, plastic bottles, children's toys, etc. (Wikipedia, 2019). In the agriculture, there are many products made from this type of plastic, such as plastic for covering the growing house to replace the clear glass and for use as plastic mulch, etc. (Bualek et al., 1991). Polylactic acid is a biodegradable plastic produced from the process of fermentation of agricultural raw materials that can be grown for renewable (Renewable resource) including flour and sugar plants as a key component. Then it will be processed through polymerization as a thermoplastic. It can be classified as thermoplastic that can be molded in many ways, such as injection molding, thermal molding, compression molding, extrusion, and blow molding, etc. Polylactic acid has properties such as clearness, brittle, stiffness, and high strength, resistance against permeability of gas and liquid similar to the plastic used in general packaging such as polystyrne (PS) or polyethylene terephthalate (PET), glass transition temperature (Tg) of 60°C, melting point at 175°C (Chotirat et al., 2007). This study carries out the analysis of heavy metals and hazardous substances in polylactic acid which is a part of the examination to confirm the quality of biodegradable plastic products according to ISO 17088: 2012. The polylactic acid plastic can be completely decomposed during fermentation according to ISO 16929: 2013 (100%) and the compost obtained from the test meets the quality required by the specific standard. (Pattanasupong et al., 2015). Assessment is carried out for the impact of compost on plants according to OECD 208 with EN 13432 Annex E using compost obtained from disintegration test during composting according to ISO 16929: 2013., the results reveal that the compost does not cause any damage to plant growth (Pattanasupong et al., 2017). Therefore, it is another alternative to use biodegradable plastic as plastic mulch for agriculture to reduce the impact on the environment

Equipment and methods

Analysis of the content of heavy metals and hazardous substances in plastics

Polylactic acid (NatureWork 2003D) and polyethylene with the size not exceeding 0.5 millimeters, will be used for analyze the amount of heavy metal and dangerous substances such as selenium, zinc, lead, cadmium, nickel, chromium

and copper by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) according to the International Electrotechnical Commission 62321 standard by the Metrology and Testing Center Thailand Institute of Scientific and Technological Research

Analysis of heavy metal content and harmful residues in the planting area

Soil samples in 5 planting areas, namely; soil from lime garden in Tha Nat sub-district, Damnoen Saduak District, Ratchaburi province for 2 samples; soil from paddy field from Khlong 4 subdistrict, and Khlong 5 subdistrict, Khlong Luang district Pathum Thani province for 2 samples and soil from banana gardens in Khlong 5 sub-district, Khlong Luang district Pathum Thani province for 1 example. These areas are selected for sampling due to lemons, rice and bananas are one of the economic crops in Ratchaburi and Pathum Thani Province (Office of Agricultural Economics, 2019). Collecting soil samples is done by digging about 15-30 centimeters deep from the soil surface before collecting the soil samples to clean the soil surface to be free from contamination. However, the sampling of soil utilizes the principle of sampling soil from many points of the same source combined together to represent the sample collection of that point. Store soil samples in the container with the lid tightly closed at 4-10°C until analysis.

Prepare the soil samples having the size not exceeding 0.5 millimeters in order to analyze the content of heavy metals and dangerous substances such as selenium, zinc, lead, nickel, chromium, and copper by weighing 0.5 grams of the soil sample, adding 9 milliliters of nitric acid and 3 milliliters of hydrochloric acid. Submerse the soil in microwave digestion at a pressure of 50 bar, the temperature of 200°C until the machine cools down for about 1 hour. Adjust the volume of the solution to 50 milliliters with the Type high purity distilled water and analyze the content of heavy metals and hazardous substances using ICP-OES machine according to the United States Environmental Protection Agency: Method 3052.

Results and Discussion

The results of the study for the content of heavy metals and hazardous substances in the polylactic acid reveal that there is the content of selenium 0.05, zinc 0.43, lead 0.12, cadmium less than 0.20, nickel, chromium, and copper less than 0.50 milligrams per kilogram. And polyethylene contains selenium 1.09. lead 0.08, cadmium 0.12, nickel 1.71, chromium 4.83, and copper for 2.21 milligrams per kilogram which are similar to those that found in Polylactic acid. And both types of plastics contain heavy metals and hazardous substances no more than the criteria according to ISO 17088 (EN 13432) standard (Table 1). In this regard, the agricultural sector has applied polyethylene in many products including plastic mulch (Bualek et al., 1991). This kind of plastic is generally known that it takes a long time to decompose naturally. Therefore there is a possibility in the application of Poly Lactic Acid to be used as mulching plastic instead of polyethylene. Since after use, the plowing can bury the plastic mulch along with compost in the planting area and it can be biodegradable by microbes. In the case of biodegradation using air, microbes will transform carbon into objects into carbon dioxide, water, salt and minerals (Katarzyna and Grazyna, 2010). The resulting product will not cause damage to plant growth. Although both types of plastic contain heavy metals and hazardous substances, not more than the stan-

Table 1 Heavy metals and hazardous substances content in plastics

Heavy metals	Acceptable criteria	Heavy metals content (mg/kg)	
	ISO 17088 (EN 13432)	PLA	PE
Se	0.75	0.05	1.09
Zn	150	0.43	N.D.
Pb	50	0.12	0.08
Cd	0.5	< 0.20	0.12
Ni	25	< 0.50	1.71
Cr	50	< 0.50	4.83
Cu	50	< 0.50	2.21

Note N.D. : Not deteced

Table 2 Heavy metals and hazardous substances content in cultivated area

Heavy metals	Soil quality standards*	Soil/Heavy metals content (mg/kg)				
	(living and agriculture)	Ratchaburi 1	Ratchaburi 2	Pathum Thani 1	Pathum Thani 2	Pathum Thani 3
Se	≤ 390	N.D.	0.31	N.D.	N.D.	N.D.
Zn	-	92.02	86.43	47.36	65.26	46.84
Pb	≤ 400	6.35	6.82	N.D.	N.D.	N.D.
Ni	≤ 1,600	32.85	4.91	22.51	25.90	20.68
Cr	≤ 300 (Hexavalent chromium)	76.05	N.D.	68.98	79.77	67.46
Cu	-	146.32	302.01	29.44	25.66	47.11

Note N.D. : Not deteced
*Pollution Control Department

dard criteria. But polylactic acid is biodegradable and does not cause damage to plant growth. The results of the study for the content of heavy metals and dangerous residues for the soil samples from Lime garden in Ratchaburi province, rice fields and banana gardens in Pathum Thani province, it is found that the soil samples in Ratchaburi province contain more zinc, lead and copper than the soil samples from Pathum Thani Province approximately 1-6 times. While the amount of nickel and chromium obtained is close to the soil samples in Pathum Thani Province. And only soil samples from Ratchaburi 2 are found to contain 0.31 milligrams of selenium per kilogram which indicates that the area of cultivation of economic crops in Ratchaburi contains more hazardous residues. This is maybe due to the relatively more usage of agricultural chemicals and that quite difficult to decompose in nature. Therefore, it can be detected in larger quantities such as insecticides in Organophosphate and Carbamate families, fungicides and herbicides (Pattanasupong et al., 2017). However, the soil samples from 5 cultivated areas contain heavy metals and dangerous substances not exceeding the standards of soil quality used for living and agriculture (Table 2). However, the soil samples in Ratchaburi Province have the content

of heavy metals and hazardous substances approximately 6-600 times more than of polylactic acid and the soil samples in Pathum Thani Province contain heavy metals are more than those of polylactic acid approximately 41-160 times. Therefore, if the application of Poly Lactic Acid is intended for use as mulching plastic, it will not have negative impacts in terms of the residue of heavy metals and dangerous substances increased in the plantation areas

Conclusion

Polylactic acid contains heavy metals and dangerous substances not exceeding the standard criteria. It can be completely decomposed during fermentation (Pattanasupong et al., 2015) and the compost obtained does not cause damage to plant growth (Pattanasupong et al., 2017) and it is found to have fewer amounts of heavy metals and harmful substances in the plantation area. Therefore, there is a possibility to use the polylactic acid which has been passed the evaluation of plastic decomposition according to ISO 17088: 2012 standard to be used as biodegradable plastic mulch for agricultural work to reduce the impact to soil and to create environmental friendliness

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