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Research article

Effect of overall migration on tensile properties of biobased plastics containing polylactic acid, thermoplastic starch and zeolite

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Abstract

Overall migration of biobased plastics were investigated. Different amounts of non-volatile substances that can migrate from food contact material or food packaging into the food were tested. Polylactic acid (PLA) and thermoplastic starch (TPS) were processed at different ratios of PLA-to-TPS of 60:40 and 80:20 with the addition of zeolite (Z5A) at 1% as a compatibilizer. Overall migration tests were conducted following The European Union Commission Regulation No. 10/2011. Migrants from the samples were extracted in food simulants using three standard testing conditions (OM1, OM2 and OM3). After extraction, the simulants were processed to determine the amounts of migrants and the samples were measured for tensile properties. Overall migration results were in the range 28.2–418.4 mg/dm^2, indicating noncompliance with the overall migration Regulation limit of 10 mg/dm^2. The testing condition at 70°C for 2 hr (OM3) showed the most promising application for food contact. Values for the tensile stress, tensile strain and Young's modulus of samples with a PLA-to-TPS ratio of 80:20 were higher than for the samples using 60:40. The Young's modulus of the sample composed of the PLA-to-TPS-to-Z5A ratio of 60:39:1 dropped to 475 MPa, while a significant reduction in tensile properties was recorded after contact with food simulants. Further investigations using lower temperatures and shorter extraction times are required to clarify the optimal conditions for commercial use.

Introduction

Food packaging and food contact materials made from biobased plastics are now in the spotlight because their environmental-friendly properties offer a sustainable way to solve problems such as waste management and depletion of petroleum that is a raw material for conventional plastics (Iwata, 2015). Polylactic acid (PLA) and thermoplastic starch (TPS) blends are biodegradable and are considered as green packaging. Furthermore, production of these materials is cost-effective with easy processing using standard equipment (Zaaba and Ismail, 2019). PLA is an aliphatic polyester whose monomer, lactic acid, derives from bacterial fermentation of carbohydrates from crops such as corn, potato and cassava

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and it is one of the most commonly used biopolymers produced on an industrial scale (Sin et al., 2012). The US FDA has approved PLA as a food contact material in 1992 (Ubeda et al., 2019).

TPS is made from agricultural products such as corn, cassava and sugarcane, as one of the most abundant polymeric materials derived from renewable resources and it is cheap, fully biodegradable and can be blended with many types of biodegradable and non-biodegradable polymers (Cai et al., 2011).

Blending of biobased materials such as PLA/TPS can enhance their physical properties and increase their durability. However, PLA and TPS are generally regarded as immiscible materials, so several strategies have been developed to improve their miscibility such as the use of compatibilizers, blending, amphiphilic molecules and coupling agents (Teixeira et al., 2012). Processing of blended polymers often encounters difficulty with homogeneity due to the hydrophobicity of PLA and the hydrophilicity of TPS; therefore, a compatibilizer such as a zeolite is added to improve the homogeneity, mechanical properties and thermal stability of the blended polymer (Thipmanee and Sane, 2012; Thipmanee et al., 2016). Zeolites are microporous crystalline aluminosilicates that because of their porosity and ability to selectively adsorb or refuse specific molecules have been widely used as absorbents for the separation and purification of gases and liquids and as a filler to improve both the physical and mechanical properties of polymers (Barthomeuf, 1996). The European Commission Regulation No. 10/2011 (The European Union Commission, 2011) does not include zeolites on its positive list, so a generic specific migration limit of 60 mg/kg applies. The USFDA has classified zeolites as GRAS (Generally Recognized as Safe) so they can be used as animal feed additives and are safe for human consumption (Eroglu et al., 2017; Fan et al., 2018).

The safety of biobased plastic should be the first consideration for its use in food contact materials. One of the most concerning issues is the migration of chemical substances from packaging material to the packed food. Chemical substances from materials in contact with products are called migrants and can be surfactants, contaminants, polymer hydrolysis by-products such as monomers, oligomers, or regulated chemical additives such as antioxidants, antimicrobials and heat stabilizers (Samsudin et al., 2018). Legislation regulates control on manufacturers and importers of food packaging to protect consumers. For example, the European Union has enacted Commission Regulation No. 10/2011 (The European Commission, 2011) to manage all plastic production and product compatibility as food contact material. Biobased plastics intended as food contact materials must also comply with this regulation. Copious research has focused on improving the physical and mechanical properties of food packaging (Din et al., 2020; Jariyasakoolroj et al., 2020; Nazrin et al., 2020). Migration testing of biobased plastic is paramount to ensure the safety of consumers. Therefore, the current study tested the migration of chemical substances from PLA and TPS biobased plastic blends using various food simulants, with the test conditions simulating the actual usage of the plastic. Mechanical properties were also investigated, as these may change in the plastic sample after migration testing. The results will assist food and packaging manufacturers to select the appropriate foodstuff intended to be in contact with the packaging and promote the safe use of biobased plastic as a food contact material.

Materials and Methods

Materials

Cassava starch was obtained from Tong Chan (Thailand) and polylactic acid (PLA, Ingeo™ 4043D) was purchased from NatureWorks LLC (USA). Glycerol (99.5% purity) was supplied by Siam Chemicals Solutions (Thailand). Zeolite 5A (Z5A) with a pore size of 4–5×10^{-10} m was supplied by Thai Silicate Chemicals (Thailand). All materials and chemicals were used as received.

Preparation of polylactic acid/thermoplastic starch/zeolite sheets using extrusion process

Thermoplastic starch (TPS) was prepared by mixing cassava starch, glycerol and Z5A. The obtained mixtures were then extruded using a twin-screw extruder (LTE-20-40; Labtech Engineering; Thailand) with a screw diameter of 20 mm and screw length-to-diameter (L:D) ratio of 40:1. The extrusion process was carried out at a temperature range of 90–160°C and screw speed of 180 revolutions per minute (rpm). The extrudate was cut to obtain TPS/Z5A pellets. The pellets were dried and melt-mixed with PLA to produce PLA/TPS/Z5A pellets at weight ratios shown in Table 1. The process used the same twin-screw extruder, operating at a temperature range of 120–160°C and screw speed of 180 rpm. The extrudate was cut into 2.5 mm length pellets, dried at 50°C overnight and subsequently extruded into sheets using a single-screw extruder equipped with a chill roll set

(CF–W400; Chareon TUT; Thailand). The extrusion process was carried out at a temperature range of 100–160°C using a screw speed of 27 rpm and upper, middle and lower casting roll speeds of 1.0 rpm, 0.5 rpm and 1.0 rpm, respectively. The thickness of the PLA/TPS/Z5A sheets was 0.7±0.1 mm.

Table 1 Weight ratios of melt mixed polylactic acid/thermoplastic starch/zeolite biobased plastic sheets

Sample	PLA	TPS	Z5A
I	60	40	0
II	60	39	1
III	80	20	0
IV	80	19	1

PLA = polylactic acid; TPS = thermoplastic starch; Z5A = zeolite 5A

Migration test

The overall migration testing was conducted according to The European Commission No. 10/2011 on plastic materials and articles intended to be in contact with food, involving both conventional and bioplastic packaging. Chemical migrants from the samples were extracted in four types of food simulants (Table 2). The extractions were conducted at the specific conditions explained in Table 3 that referred to the worst foreseeable testing conditions of the intended usage in Annex V of The European Commission (No. 10/2011). After the extraction, a known aliquot of extracted simulant was evaporated to dryness and the remaining extractable substances or migrants were weighed. Each food simulant was placed in separate beaker to perform blank samples. All experiments were done in triplicate. The results of the overall migration were reported as the average quantity of migrants in micrograms per square decimeter of the sample.

Tensile test

Tensile properties (tensile stress, elongation at break, Young's modulus) of the samples were measured according to the ASTM D882 Standard Test Method for Tensile Properties of Plastics (ASTM International, 2018). The samples were measured using an electronic tensile strength meter (5965; Instron; USA) equipped with a 5 kN load cell, a crosshead speed of 50 mm/min and a gauge length of 50 mm. The specimens were prepared by contact with the food simulants under the same conditions for the overall migration testing. This preparation represented the actual usage of the bioplastic sheet. Specimens without the preparation were the control samples.

Statistical analysis

The results of the overall migration test and tensile test were subjected to one-way analysis of variance using the SPSS Statistics software version 28.0.0.0 (190). Statistical significance of the difference between mean values was determined using Duncan's new multiple range test at $p < 0.05$.

Table 2 Food simulants for migration testing

Food simulant	Abbreviation	General assignment of food simulants to foods
Ethanol 10 % (v/v)	Food simulant A	Foods that have a hydrophilic character and can extract hydrophilic substances that have a pH above 4.5
Acetic acid 3 % (w/v)	Food simulant B	Foods that have a hydrophilic character and can extract hydrophilic substances that have a pH below 4.5
Ethanol 20% (v/v)	Food simulant C	Alcoholic foods with an alcohol content of up to 20% and those foods which contain a relevant amount of organic ingredients that render the food more lipophilic
Ethanol 50% (v/v)	Food Simulant D1	Foods that have a lipophilic character and can extract lipophilic substances. Alcoholic foods with an alcohol content above 20% and oil in water emulsions

v/v = volume per volume; w/v = weight per volume

Table 3 Standardized conditions for overall migration testing

Test number	Contact time and temperature	Intended food contact conditions
OM1	10 d at 20°C	Any food contact under frozen and refrigerated conditions.
OM2	10 d at 40°C	Any long term storage at room temperature or below, including heating up to 70°C for up to 2 hr, or heating up to 100°C for up to 15 min.
OM3	2 hr at 70°C	Any contact conditions that include heating up to 70°C for up to 2 hr, or up to 100°C for up to 15 min, that are not followed by long term room or refrigerated temperature storage.

Results and Discussion

Overall migration

The overall migrations of biobased plastics extracted under the intended application conditions (OM1, OM2, OM3) are shown in Fig. 1. The main factors of the migration were the different conditions that simulated the worst foreseeable condition of use for the biobased plastics. In Fig. 1A, the OM1 samples were tested at 20°C for 10 d, imitating the worst conditions in the freezer and refrigerator. The overall migration results were in the range 57.3–367.4 mg/dm^2, while results from the OM2 testing condition (Fig. 1B) increased the range to 90.32–418.4 mg/dm^2 due to the more severe conditions at 40°C for 10 d that imitated long term storage at room temperature or below, including heating up to 70°C for up to 2 hr or heating up to 100°C for up to 15 min. However, the results from OM3 (Fig. 1C) involving heating at 70°C for 2 hr, decreased the range to 28.3–290.1 mg/dm^2. The OM3 case simulated conditions for intended food involved heating up to 70°C for up to 2 hr or up to 100°C for up to 15 min, that were not followed by long term room or refrigerated temperature storage. All the results from these biobased plastics were higher than the overall migration limit of 10 mg/dm^2. The most promising application under OM3 condition that resembled the application of single-use plastic food containers such as coffee cups, cutlery and tableware for street foods.

The different type of simulants did not affect overall migration under OM1 and OM2. The extraction period (10 d) for these conditions was long enough to reach the extraction equilibrium. However, under OM3, variations in migration were evident among the types of simulants. Extraction with simulant D1 (50% ethanol) produced the highest migration. Such biobased plastics would be most unsuitable for contact with foods having a lipophilic character, alcoholic foods with an alcohol content above 20% and oil in water emulsions. Simulant C (20% ethanol) also produced a high value of overall migration, which indicated incompatibility between biobased plastics and alcoholic foods with an alcohol content up to 20%, and foods that contained a relevant amount of organic ingredients that rendered the food more lipophilic. Promising conditions of use for this biobased plastic were extraction with simulant A and simulant B that produced relatively low levels of overall migration. Thus, under short term application (OM3), bioplastic samples were more appropriate for use with foods that had a hydrophilic character. Lower results were noticeable at a higher ratio of PLA in samples III (PLA:TPS = 80:20) and IV (PLA:TPS: Z5A = 80:19:1), with less effect of starch from TPS on the migration results.

In the PLA/TPS biobased plastics, TPS was added to improve the tensile properties and reduce the production cost. However, a higher weight ratio of TPS resulted in increased numbers of migrants due to the hydrophilicity of TPS.

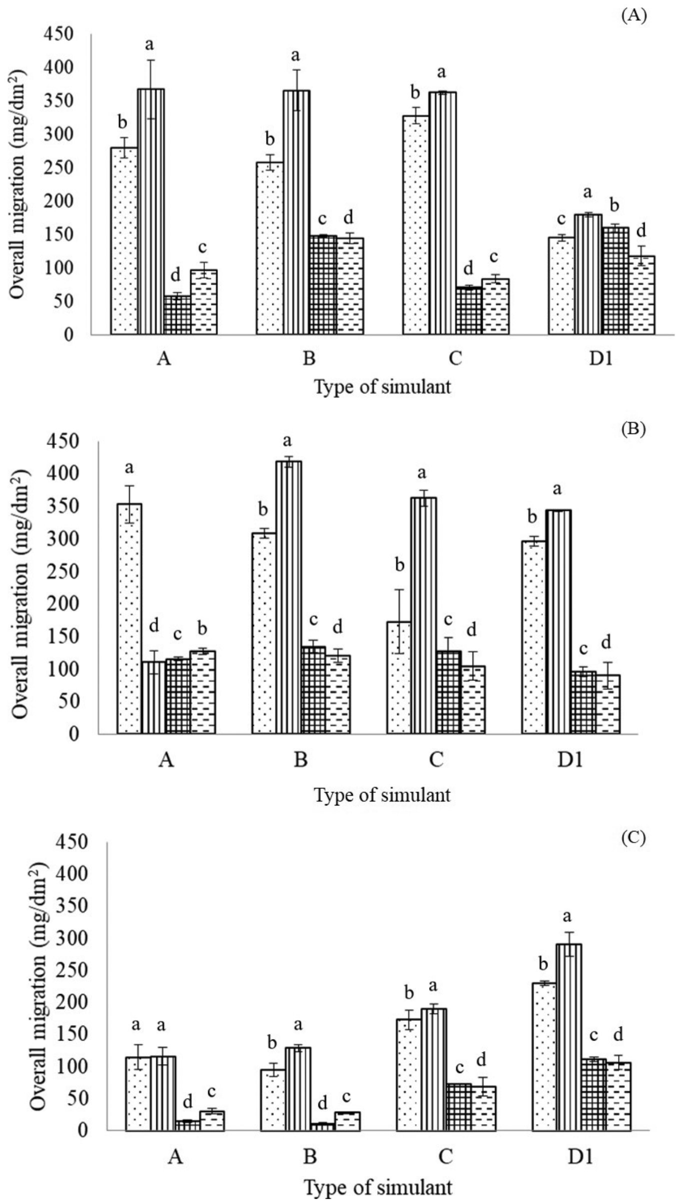

Fig. 1 Overall migration of biobased plastic under three standardized testing conditions: (A) OM1; (B) OM2; (C) OM3, for Sample I ( ), Sample II ( ), Sample III ( ) and Sample IV ( ), where error bars represent SD and different lowercase letters above bars indicate significant ($p < 0.05$) differences within simulants (defined in Table 2) and OM1, OM2 and OM3 are different testing conditions defined in Table 3

The starch and glycerol contents in TPS increased the overall migration for samples I and II, with higher results than for samples III and IV under most of the testing conditions and types of simulants.

The addition of 1% Z5A as a compatibilizer in PLA/TPS/Z5A was used to improve the mixing process of the biobased plastic. However, the overall migration result showed that the sample with Z5A had higher migration compared to the sample without Z5A at the same ratio of TPS. Zeolites reduced the size of TPS in the dispersed phase in the materials and improved the spatial distribution and decreased the agglomeration of the TPS domain (Thipmanee et al., 2016; Yimnak et al., 2020). Thus, the simulants accessed more TPS and caused greater migration in the sample with Z5A.

The physical appearance of the biobased plastics changed after contact with the food simulants. Samples I and II, both containing less PLA, showed greater deformation compare to samples III and IV. The PLA provided strength to the biobased plastics to improve deformation resistance. The addition of Z5A as a compatibilizer did not affect the deformation of samples. Fig. 2 shows the deformation of the samples that were tested under OM3 with simulant B (3% acetic acid).

Tensile properties

The tensile stress, elongation at break and Young's modulus of the biobased plastic samples were measured without any contact with food simulants as control samples, and after contact with four types of food simulants. Fig. 3A shows the tensile stress of the biobased plastics. Tensile stress is the resistance of an object to a force tending to tear it apart and samples with higher tensile stress are harder to tear as they are stronger (MatWeb, n.d.). Samples after contact with food simulant D1 (50% ethanol) produced the maximum reduction in tensile stress of all tested samples. The incompatibility of simulant D1 representing oily foods was shown by its highest overall migration. For samples I and II, the average values reduced from 29.4 MPa to 9.1 MPa, while the average value of samples III and IV reduced from 33.6 MPa to 16.1 MPa. Thus, samples III and IV with 80% PLA were stronger than samples I and II with 60% PLA. This tendency has been reported in many blends such as PLA/TPS and polyethylene (PE)/TPS (Thipmanee et al., 2016), linear low-density polyethylene (LLDPE)/TPS (Thipmanee and Sane, 2012) and poly(butylene-adipate-co-terephthalate) (PBAT)/TPS (Lackner et al., 2021) where a higher percentage of TPS decreased the tensile stress of the material.

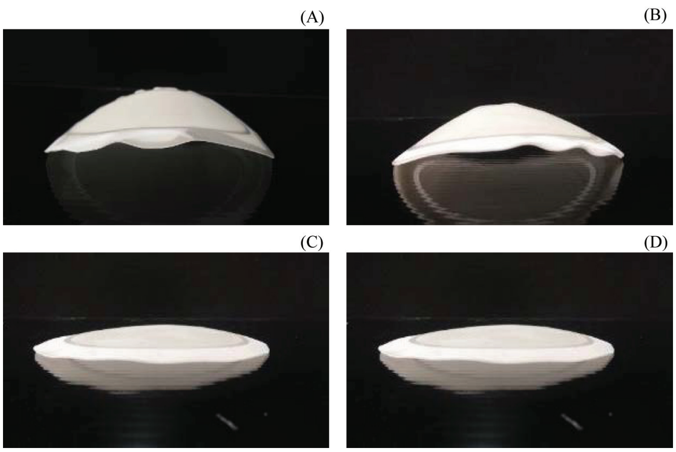

Fig. 2 Physical appearance of biobased plastic after contact with simulant B (3% acetic acid) under OM3 conditions: (A) polylactic acid (PLA):thermoplastic starch (TPS) = 60:40; (B) PLA:TPS:Z5A = 60:39:1; (C) PLA:TPS = 80:20; (D) PLA:TPS:Z5A = 80:19:1

Elongation at break of the biobased plastics is shown in Fig. 3B as the ratio between the increased length and initial length after breakage of the tested specimen at a controlled temperature. This measure is related to the ability of a plastic specimen to resist changes of shape without cracking, as the elasticity of the sample. In the control samples, the values for elongation at break of samples I and II were higher than for samples III and IV. A higher amount of PLA resulted in a lower elongation at break due to the high glass transition temperature (Tg) of PLA, while TPS produced a higher elongation at break because of the presence of plasticizer molecules (Esmaeili et al., 2019). However, samples after contact with food simulants showed adverse results. The effects of food simulants on the biobased plastics were different depending on the ratio of PLA-to-TPS. The elongation at break of samples I and II decreased after contact with food simulants, while samples III and IV had increased elongation at break after contact. The hydrophilic TPS absorbed food simulants and reduced the elongation at break. However, the different types of food simulants did not affect the results.

Young's modulus is a measure of the ability of a material to withstand changes in length when under lengthwise tension or compression and a higher Young's modulus value indicates less deformation (MatWeb, n.d.). Fig. 3C shows the Young's modulus values of the biobased plastic samples, with samples III and IV with higher ratios of PLA had higher Young's modulus values or greater stiffness. These results followed the rule of mixtures, as a more flexible and ductile polymer (TPS) added to a rigid polymer (PLA) will lower the Young's modulus value (Turco et al., 2019). This shift in Young's modulus values after contact with food simulants was found in all samples. The Young's modulus values of samples I and II decreased after contact with food simulants, but for samples III and IV it increased. PLA caused greater stiffness in the samples and withstood deformation after contact with food simulants representing actual usage of the biobased plastics. The results for the deformation of the samples are shown in Fig. 2.

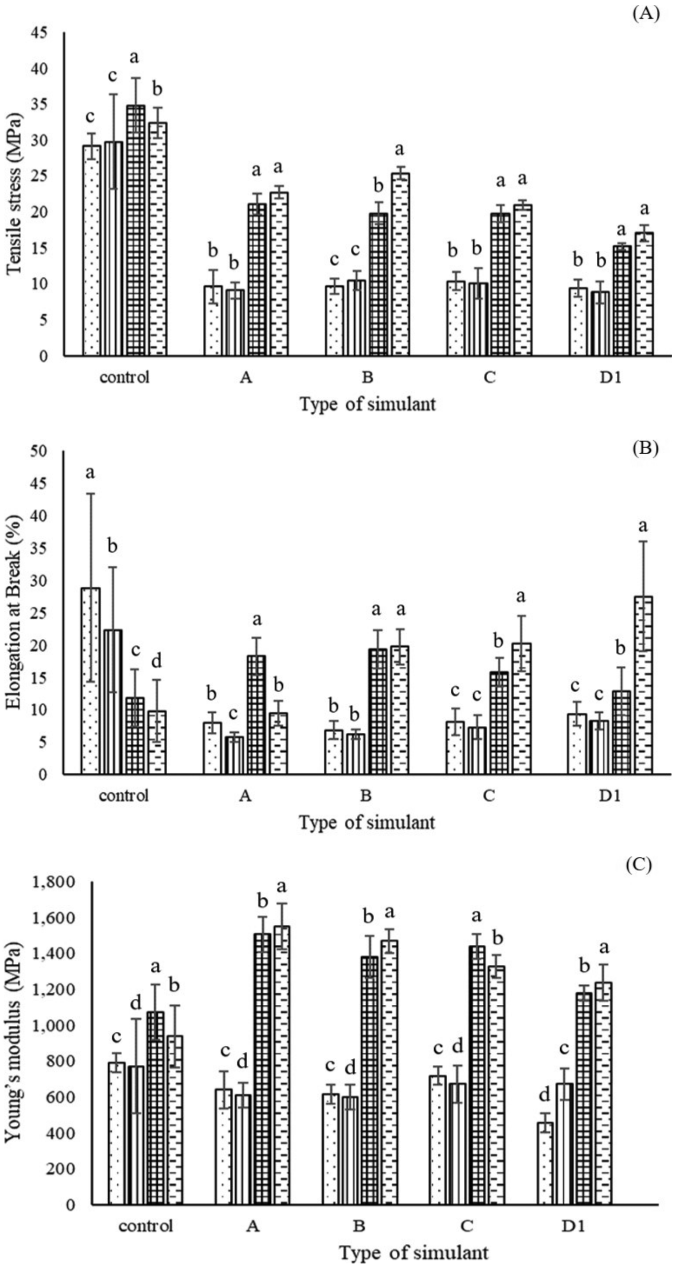

Fig. 3 Tensile properties of biobased plastic after contact with simulant B (3% acetic acid) under OM3 conditions: (A) tensile stress; (B) elongation at break; (C) Young's modulus, for Sample I ( ), Sample II ( ), Sample III ( ), Sample IV ( ), where error bars represent SD and different lowercase letters above bars indicate significant ($p < 0.05$) differences within simulants (defined in Table 2) and OM3 testing conditions are defined in Table 3

Glycerol and sorbitol were added to the TPS phase to formulate a finer morphological blend with higher tensile strength and Young's modulus (Li and Huneault, 2010; Nazrin et al., 2021). However, in the current study, there was no distinct effect of Z5A as a compatibilizer on the tensile properties of samples after contact with food simulants.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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