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Biodegradation and Anti-bacterial Properties of PLA and Wood/PLA Composites Incorporated with Zeomic Anti-bacterial Agent

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Abstract. Anti-bacterial and biodegradation activities of Poly(lactic acid) (PLA) and wood flour/PLA composites (WPLA) were investigated for the effect of anti-bacterial agent addition. Silver substituted Zeolite (commercially designated as Zeomic) was used as anti-bacterial agent in this study. Anti-bacterial activities were investigated through dynamic shake flask method accompanying with plate count agar (PCA) technique, against *Staphylococcus aureus* as testing bacteria. The results of anti-bacterial activity were reported by viable cell count. For biodegradation test, the degree and rate of biodegradations were evaluated from percentage of carbon conversion, the test being carried out under laboratory controlled-aerobic degradation environment at a temperature of 58±2°C. The results found that addition of Zeomic did not perform anti-bacterial activities for both the neat PLA and WPLA due to non-diffusivity of silver in Zeomic. For biodegradation test, both PLA and WPLA samples during incubation times of 21-60 days had shown considerable biodegradation rates as a result of chain scission by hydrolysis reaction and subsequent enzymatic-biodegradation by microorganism of PLA molecules. Regarding the effect of wood and Zeomic addition, it was found that introducing wood and Zeomic in PLA matrix tended to markedly increase the degree and rate of biodegradation of PLA and WPLA materials, whereby the PLA having 10%wt of wood with 1.5%wt of Zeomic had the most satisfactory biodegradation level and rate as a consequence of accelerated hydrolysis degradation from moisture in wood and Zeomic.

Introduction

Nowadays environmental and health problems are of concern for human life. Material selection accompanying with disposal-ability of materials after their uses in appropriate ways are gaining popularity and attention form many researchers [1-5]. Poly(lactic acid) (PLA) is one of the most common biodegradable plastics for food packaging applications, which is the largest volume of plastic materials consumption. The use of PLA materials concerns hygienic purposes and safety from food pathogen. To accommodate the prevention of bio-contamination and biodegradable properties of PLA, anti-microbial and biodegradation properties on PLA materials would be worth investigating.

According to the discoveries by the previous studies [2-4] revealed that anti-microbial properties as well as the biodegradation process of materials were influenced by the biodegradable reinforcing fillers like wood [2]. Adding wood in PLA materials was found to enhance the bio-deterioration by microorganisms [3] and also promote the anti-bacterial effect [4]. Based on existing literatures, none of the published evidence has studied the anti-microbial activities by means of anti-microbial performance and degree of biodegradation of PLA and wood/PLA composites (WPLA). The contradiction effects between adding anti-microbial property (for hygienic purpose) and biodegradability by adding decomposable filler like wood (for bio-decomposable purpose) of PLA (biodegradable materials) would be very attractive and still unclear, but open for wide discussion.

Therefore, in this study, the effect of wood and anti-bacterial agent additions on anti-bacterial properties and biodegradations of PLA were investigated. Silver substituted zeolite, known as Zeomic was used as an anti-bacterial agent. Biodegradation test by ASTM D3558 and dynamic shake flask method (accompanying with plate count agar (PCA) technique) using *Staphylococcus aureus* as testing bacteria were used for evaluations of degree of biodegradation and anti-bacterial performances of materials, respectively.

Experimental

Materials and chemicals: Poly(lactic acid) or PLA (2003D, NatureWorks, USA) was used as a polymer matrix. Commercial biocide, Silver substituted zeolite or Zeomic (supplied by Yamamoto Trading Co., Ltd., Thailand) was used as anti-bacterial agent. Wood flour having an average particle size ranging from 100 and 300 μm (supplied by V.P. Wood Co., Ltd., Bangkok, Thailand) was used and chemically surface-treated by silane coulpling agent (KBM 603, Shin-Etsu Chemical Co. Ltd., Japan) before introducing into PLA material.

Specimen preparation: All raw materials were mixed using a high speed mixer and subsequently twin screw extruder (Haake Polylab-Rheomex CTW 100P, Germany) in order to possess the PLA compounding in form of pellets. All raw materials and the compounding were then dried at 70^{o}C for 24 hrs for moisture removal. The PLA compounds was finally hot-pressed under processing temperature, compression pressure and holding time of 170^{o}C, 150 kg/cm^2 and 5 min, respectively, before being cold-pressed until the temperature reached 25^{o}C (approx. 5 min).

Anti-bacterial activity: Evaluation of anti-bacterial activities was carried out through dynamic shake flask method accompanying with plate count agar technique, using *S. aureus* (ATCC 25923) as a testing bacteria. The procedure of this method can be obtained by our previous work [3]. The results were reported in terms of colonies forming unit per milliliter (cfu/ml) with varied contact times (0-4 h). Anti-bacterial properties of materials were accounted by comparative analysis of viable cell count from treat and untreated PLAs by means of bactericidal behavior.

Biodegradation test: Testing procedures as well as the apparatus sets for biodegradation test followed ASTM D5338 method which determines the degree and rate of aerobic biodegradations of plastic materials on exposure to a controlled-composting environment under laboratory conditions under thermophilic temperatures (58±2°C), by which the test inoculum is derived from the compost of municipal solid waste. Yields (%) of conversion of carbon in the sample to carbon dioxide (CO_2) were accounted for the rate and level of biodegradations. The experimental apparatus setting is shown in Fig. 1.

Figure 1 Set of experimental apparatus for bio-degradation test by soil-composting test as followed by ASTM D5338

Results and discussion

Fig. 2 demonstrates the results of anti-bacterial evaluations for PLA and WPLA samples. Reduction of viable cell count with contact time indicates bactericidal effect of materials. It can be seen that the number of viable cell count increased with increasing contact time for both PLA and WPLA specimens. This applied to both PLA and WPLA samples with and without Zeomic. Therefore, it could be said that Zeomic could not kill *S. aureus* in PLA and WPLA samples. This may be expected because of difficulties in diffusing of silver particle or silver ion from Zeomic [5].

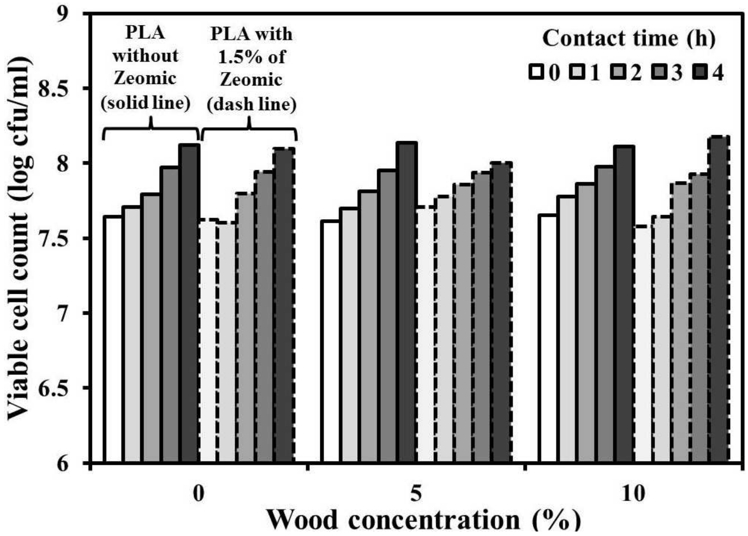

Figure 2 Viable cell count of *S. aureus* along with contact time for PLA without (solid line) and with 1.5 %wt of Zeomic (dash line) at different wood contents

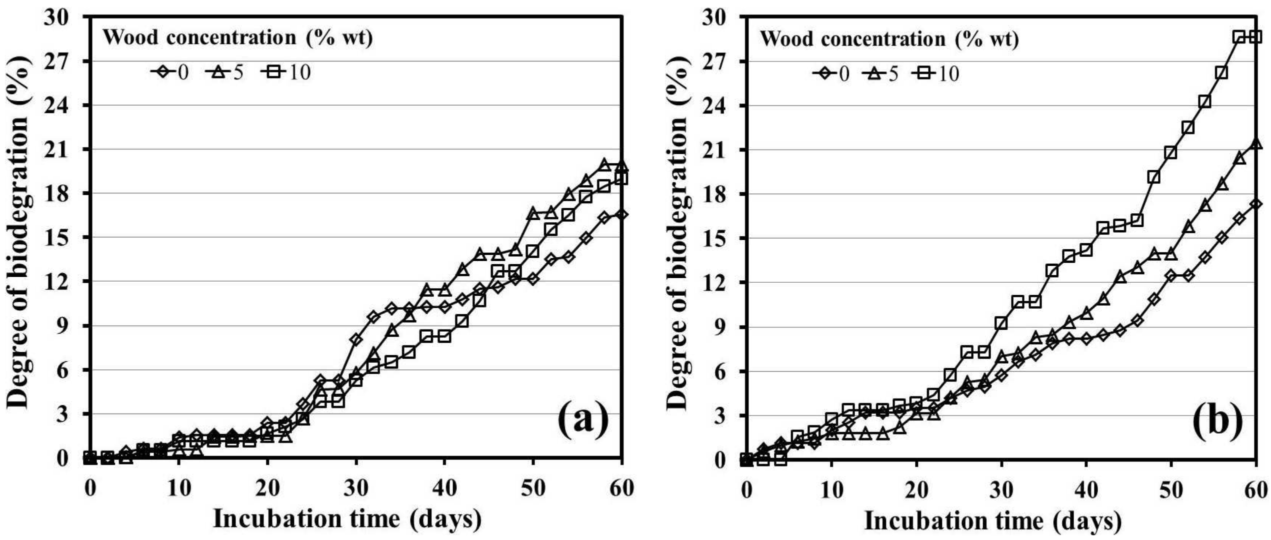

Figure 3 Degree of biodegradations for PLA without (a) and with 1.5%wt of Zeomic (b) at different wood contents

Table 1 Rate of biodegradations of PLA for the effects of wood and Zeomic additions

Incubation time (days)	Wood concentration (% by wt.)					
	0	5	10	0	5	10
	Zeomic concentration (% by wt.)					
	0.0			1.5		
0-20	0.110	0.091	0.082	0.178	0.121	0.222
21-60	0.319	0.491	0.461	0.339	0.455	0.630

For biodegradation test, the degree and rate of biodegradations of PLA with different wood concentrations are shown in Fig. 3 and Table 1, respectively. It can be noted that adding wood in PLA had a tendency of increasing degree of biodegradation. This effect was more pronounced in the case of addition of Zeomic. The degree of biodegradation for 60 days of incubation time for PLA with 0, 5 and 10%wt wood were 16.6-17.3%, 20.0-21.5% and 19.0–28.6%, respectively for the loading of Zeomic at 1.5%wt. The explanation would be attributed to more hydrolysis degradation of PLA due to presence of moisture in wood and Zeomic. The hydrolyzed PLA molecules were easier to degrade as compared with the neat or non-hydrolyzed ones.

Regarding the rate of biodegradation (Table 1), it can be noticeable that the rates of biodegradations of PLA samples for incubation time during 21-60 days were significantly faster than those during 0-20 days. These phenomena would suggest that during the first soil-compositing period (0-20 days), the PLA molecules could retard the hydrolysis reaction as a result of long chain molecules and partial crystalline portion of PLA, which prevented the PLA molecules from water molecules penetration and subsequent stimulation of the hydrolysis reaction. On the other hand, for the latter period (21-60 days), it is believed that under the thermophilic conditions (58 ± 2°C) accompanying with high humidity environment leading to deteriorate the crystalline structure, more hydrolysis and chain scission reactions of PLA molecules had become pronounced. As a result, the further enzymatic biodegradation caused by microorganism to yield carbon element from biodegradation process had then occurred. It was interesting to note that the maximum rate of biodegradation was obtained for the WPLA with 10%wt of wood and 1.5%wt of Zeomic.

Summary

Anti-bacterial performances in both PLA and WPLA formulations were not found by addition of Zeomic. The biodegradation test revealed that the additions of wood and Zeomic had a synergetic effect on biodegradations in PLA. Under the laboratory controlled-aerobic degradation environment and thermophilic temperatures (58±2°C) by ASTM D3558, the degradation of PLA involved the hydrolysis reaction and subsequent enzymatic-biodegradation by microorganism. The rate of biodegradation of PLA and WPLA materials were pronounced after 20 days of incubation time. In this study, the highest degree and rate of biodegradation reaction of the PLA were yielded when introducing the wood at 10 %wt and Zeomic at 1.5%wt.

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