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To cite this article: C Prapruddivongs et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 244 012007

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Effect of commercial SiO$_2$ and SiO$_2$ from rice husk ash loading on biodegradation of Poly (lactic acid) and crosslinked Poly (lactic acid)

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Abstract. In this work, biodegradation behavior of poly (lactic acid) (PLA) and crosslinked PLA filled with two types of SiO$_2$, precipitated SiO$_2$ (commercial SiO$_2$) and SiO$_2$ from rice husk ash, were studied. Rice husks were first treated with 2 molar hydrochloric acid (HCl) to produce high purity SiO$_2$, before burnt in a furnace at 800º C for 6 hours. All components were melted bending by an internal mixer then hot pressed using compression molder to form tested specimens. FTIR spectra of SiO$_2$ and PLA samples were investigated. The results showed the lack of silanol group (Si-OH) of rice husk ash after steric acid surface modification, while the addition of particles can affect the crosslinking of the PLA. For biodegradation test by evaluating total amount of carbon dioxide (CO$_2$) evolved during 60 days incubation at a controlled temperature of 58± 2° C, the results showed that the biodegradation of crosslinked PLA occurred slower than the neat PLA. However, SiO$_2$ incorporation enhanced the degree of biodegradation. In particular, introducing commercial SiO$_2$ in PLA and crosslinked PLA tended to clearly increase the degree of biodegradation as a consequence of the more accelerated hydrolysis degradation.

1. Introduction

Biodegradable polymers, such as poly (lactic acid) (PLA) [1-2], polyhydroxybutyrate (PHB) [3-4], cellulose [5-6] have been becoming increasingly popular. Among these, PLA is the most attractive polymers for further improvement because of its high mechanical strength, biocompatibility, biodegradability and processability facilitating the PLA to be used for much applicability [7-8]. However, the low thermal stability restricted the PLA in some applications [9]. In order to overcome the drawback, many technics, for example, creating crosslinking structures [10], forming composites [11-12] and chain extension [13] were employed. The electron beam irradiation associated with triallyl isocyanurate (TAIC) was normally utilized to form PLA crosslinking structures, resulting in an improvement of thermal stability of the PLA [14]. The inclusion of chemical crosslinking agent either TAIC and DCP at small dosage can also increase gel fraction and crosslinking density of the PLA [10]. Incorporation of SiO$_2$ 1.5 wt% improved thermal stability of the PLA/SiO$_2$ composites approximately 20 °C as a result of a decrease in spherulite dimension causing an increase of crystallinity [15]. Enhancement of the thermal property and crosslinking structure can affect the biodegradation rate of the PLA. Thus, this work aimed to study the
effect of SiO₂ loading, commercial SiO₂ and SiO₂ from rice husk ash, on the biodegradation of PLA and crosslinked PLA (CrPLA).

2. Experimental

2.1. Materials and chemicals
Poly(lactic acid) (PLA, 2003D, by NatureWorks, USA) was used in this work. Triallyl isocyanurate (TAIC) and dicumyl peroxide (DCP) were supply by PI industry Co. (Bangkok, Thailand). Synthetic precipitated silica was purchased from OSC Siam Silica (Bangkok, Thailand). Stearic acid (B18010 by, Kuala Lumpur Kepong Bhd, Malaysia) was used to modify surface of silica.

2.2. Silica preparation
Rice husks 100 g were cleaned by washing with tap water 3 times before soaking in 1 L of 2 M HCl solution for 4 hours. The husks were dried at 100°C for overnight in an oven after washing with tap water until pH was 7. Next, the dried husks were burnt at 800 °C for 6 hours. The rice husk ashes (RHSiO₂) and commercial silica powder (CSiO₂) were milled for 12 hours and sieved to select the SiO₂ size under 75 µm. Finally, silica were modified surface using stearic acid soluted in isopropyl alcohol. The ratio of stearic acid and silica was 1:10. After the surface treatment, SiO₂ (CSiO₂ and RHSiO₂) were dried 12 hours before mixing with PLA.

2.3. Specimen preparation
PLA was dried at 80°C for 3 hours to remove moistures. All components including PLA, RHSiO₂, CSiO₂, TAIC and DCP were-melt bending using an internal mixer (MX500-TQ, Chareontut, Thailand) to produce PLA and crosslinked PLA composites. The ratio of chemical crosslinking agent TAIC and DCP used was 0.5:0.5 weight percent. Testing specimens were formed by compression molded at 190 ºC for 5 min.

2.4. Biodegradation test
The set apparatus for biodegradation test was applied from ASTM D5338 to determine the degree of biodegradations. In order to maintain thermophilic condition, temperature was controlled at 58±2°C throughout 60 days of the test. Carbon dioxide (CO₂) occurred were reacted with Barium hydroxide (Ba(OH)₂) solution. Then, the degree of biodegradation was defined by titration with hydrochloric (HCl). The schematic apparatus is shown in Figure 1.

3. Characterizations
An attenuated total reflectance mode Fourier transform infrared spectroscopy (FTIR; Spectrum Spotlight 300, PerkinElmer, USA) was performed to examine surface treatment of SiO₂ and chemical crosslinking of PLA composites filled TAIC and DCP.

Figure 1. Schematic apparatus for aerobic biodegradation test
4. Result and discussion

FTIR of CSiO$_2$ and RHSiO$_2$ before and after surface treatment are given in Figure 2. FTIR spectrum of pure CSiO$_2$ appeared at about 3500 cm$^{-1}$, 1100 cm$^{-1}$ and 950 cm$^{-1}$ which belong to hydroxyl (-OH), siloxane (Si-O-Si) and silanol (Si-OH), respectively. Spectrum of pure RHSiO$_2$ was similar to the spectrum of CSiO$_2$. After stearic acid surface treatment, silanol group at about 950 cm$^{-1}$ for CSiO$_2$ still remained. However, the silanol peak disappeared for treated RHSiO$_2$ indicating the reaction between carboxylic group (-COOH) and hydroxyl group (-OH) performed well. This disappearance confirms the accomplished coat of stearic acid on RHSiO$_2$ surface. Figure 3 shows FTIR spectra of pure PLA and chemical crosslinked PLA (CrPLA) with the addition of 4 wt% treated SiO$_2$. The carbonyl (C=O) stretching peak of PLA happened at the wavenumber of 1750 cm$^{-1}$. The incorporation of chemical crosslinking agents appeared a new peak at about 1690 cm$^{-1}$ which clearly insists the crosslinking of TAIC and PLA [16]. However, the peak became unclear for 4RHSiO$_2$CrPLA and 4CSiO$_2$CrPLA. This suggested a decrease in crosslinking level of CrPLA in the presence of RHSiO$_2$ and CSiO$_2$.

![Figure 2](image2.png)

**Figure 2.** FTIR spectra of pure CSiO$_2$, RHSiO$_2$, treated CSiO$_2$ and treated RHSiO$_2$

![Figure 3](image3.png)

**Figure 3.** FTIR spectra of PLA, CrPLA, 4RHSiO$_2$CrPLA and 4CSiO$_2$CrPLA
The degrees of biodegradation of PLA and crosslinked PLA composites are shown in Figure 4. It can be seen that all tested samples biodegraded increasingly upon the incubation time. The first 20 days of the test, the sample degraded slowly. This would imply that the long chain and high molecular weight of PLA could prevent water molecules to penetrate retarding hydrolysis reaction to occur. For later phase (21-60 days), biodegradation began rapidly. The more water molecules could penetrate; the more hydrolysis reaction would occur. The crosslinked samples slowed down the degree of biodegradation. The crosslinking reaction created dense PLA chains retraining the PLA to be hydrolyzed. It can be observed that added SiO₂ in PLA and CrPLA displayed enhancing degree of biodegradation. This effect was more remarkable for CSiO₂. After 60 days of testing, the degree of biodegradation of PLA, 1RHSiO₂PLA and 1CSiO₂PLA were 56.8%, 58.8% and 70.1%, respectively. The FTIR of SiO₂ surface modification (Figure 2) displayed successful surface treatment of stearic acid onto RHSiO₂ surface causing less hydrophilicity of RHSiO₂. The hydrophilicity played a key role in facilitation of the PLA as well as crosslinked PLA to be hydrolyzed.

Figure 4. Degree of biodegradation for PLA (a) and CrPLA (b) with 1wt%RHSiO₂ and 1wt%CSiO₂ loading.
5. Conclusion
In this work, biodegradation behavior of poly (lactic acid) (PLA) and crosslinked PLA filled with precipitated SiO\textsubscript{2} (commercial SiO\textsubscript{2}) and SiO\textsubscript{2} from rice husk ash, were studied. FTIR spectra of SiO\textsubscript{2} showed the lack of silanol group (Si-OH) of RHSiO\textsubscript{2} after steric acid surface modification suggesting the accomplished coat of stearic acid on RHSiO\textsubscript{2} surface. The addition of SiO\textsubscript{2} particles affected the crosslinking of the PLA. Biodegradation of crosslinked PLA occurred slower than the neat PLA. However, SiO\textsubscript{2} incorporation enhanced the degree of the degradation. In particular, introducing commercial SiO\textsubscript{2} in PLA and crosslinked PLA tended to clearly increase the degree and rate of biodegradation as a result of hydrophilicity.

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Acknowledgement
The authors would like to thank King Mongkut’s University of Technology North Bangkok (KMUTNB) for research funding. Contract no. KMUTNB-60-GOV-40.