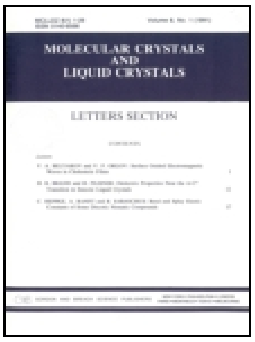

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Fabrication of Controlled Surface Properties of Poly(L-lactide) by Mixing with Lotus Leaf Powder

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A biocompatible polymer composite film was prepared by casting method of the mixed solution of poly(L-lactide) (PLA) and lotus leaf powder (LLP) in chloroform. The obtained composite film showed hydrophobic properties. The surface wettability and change in the surface morphology of the film before and after degradation in the enzyme solution were analyzed by contact angle measurement and high resolution scanning electron microscopy. The degradation rate of PLA could be controlled by mixing the right composition of LLP to PLA.

Keywords Poly(L-lactide); Lotus leaf powder; Wettability; Enzyme; Degradation rate

Introduction

Recently bio-based polymers are used potentially in several applications such as tissue engineering, drug delivery, cancer therapy, wound-healings, cell adhesion, etc [1,2]. The key advantages of bio-polymers over the synthetic polymers are the biocompatible, non-toxic, and biodegradable properties in the simulated body fluids or in soil. The biodegradability is mainly due to the presence of hydrophilic functional groups in the bio-polymers. Poly(L-lactide) (PLA) is a widely used biopolymer for several applications due to the excellent properties [3]. It has been reported that the biodegradability of PLA is controlled by the addition of other biopolymers or materials by compounding or blending method. Also, the obtained sample can enhance thermal stability and flexibility based on a component used in the synthesis or preparation.

The main objective of this work is to control the degradation rate of PLA. This could be achieved by the addition of hydrophobic materials to the PLA. Lotus leaf (LL) is well known superhydrophobic substrate by its self-cleaning behavior [4]. The superhydrophobicity of LL is due to the presence of micro-nano hierarchical surface roughness and the hydrophobic waxy materials on the leaf surface. The LL powder (LLP) also show hydrophobicity under

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Table 1. Compositions of pristine PLA and PLA/LLP composite films

Sample	P100	P99.4	P99	P98
PLA (g)	1.5	1.5	1.5	1.5
LLP (g)	-	0.010	0.015	0.030

various solvents [5]. In this work, we prepared controlled biodegradable PLA composite films by mixing LLP with PLA by solution mixing method. The biodegradability of the PLA composite films were studied by enzyme in a buffer solution.

Experimental

PLA (grade: 4032D, L-lactic acid/D-lactic acid: 98.6/1.4) with an average molecular weight of 200,000 was purchased from Natureworks LLC. Chloroform was bought from Junsei Chemicals. Each solution of LLP and PLA in chloroform was separately prepared. LLP solution was prepared by stirring (1000 rpm for 12 h) the LLP (0.5 g) in chloroform (250 mL) followed by filtering the dispersion using filter paper (mixed cellulose esters membrane filter, 0.5 μm). The details of LL and LLP solution were reported elsewhere [5]. The mixture solutions were prepared from each solution, cast on the glass substrate and dried at 60°C for 24 h. The characteristics of composites used in the study are shown in Table 1. The surface wettability of the coated glass substrates were measured by drop shape analysis system (DSA 100, Krüss GmbH). The static contact angle (SCA) was measured using 500 μL syringe and a needle, 0.5 mm in diameter and 38 mm in length and liquid (water) volume of 3 μL at a flow rate of 600 rpm [5]. The surface morphology of the samples at before and after enzymatic degradation were analyzed using high resolution scanning electron microscopy (HR-SEM, TESCAN (Czech) Vega II LSU). The samples were coated with platinum prior to the measurement. For enzymatic degradation test, the coated glass substrates were soaked in to 2 mL of tris-HCl buffer solution followed by the addition of 0.04 mL of 5 mg/mL proteinase K solution. Tris-HCl buffer solution was prepared by tri(hydroxymethyl)aminomethane (99.8+%, Sigma-Aldrich). The pH of buffer solution (pH 8.5) was controlled by HCl. The degradation test was performed by incubation of the samples in the buffer solution at fixed temperature (37.5°C).

Results and Discussion

Fig. 1 shows the SCA images and its values of pristine PLA and PLA/LLP composite films. The pristine PLA (P100) coated glass substrate showed the hydrophilic (82.77° ± 2.0°) property (Fig. 1a). The hydrophilic property of the PLA substrate is mainly due to the hydrophilic hydroxyl and ester groups in the PLA networks surface which nucleates the water droplet partially on the substrate due to the hydrogen bonding of water molecule with the surface functional group [4]. The prepared PLA/LLP composite film (P99.4) showed the hydrophobic property (103.69° ± 1.5°) (Fig. 1b). Owing to the hydrophobic property of LLP, the PLA/LLP composite film substrate became stable hydrophobic property. The surface property of the film was also checked by increasing the LLP contents (Fig. 1c and 1d). The prepared films showed the enhanced surface properties (105.79° ± 1.0° and 114.28° ± 2.0°) due to the excess of hydrophobic LLP contents (Figs. 1c and 1d).

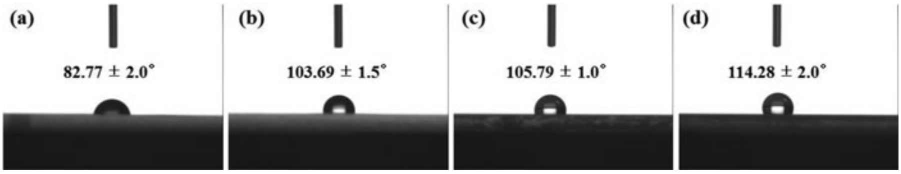

Figure 1. Optical images for the static contact angle of pristine PLA and PLA/LLP composite films. (a) pristine PLA, (b) PLA/LLP 99.4/0.6 by wt%, (c) PLA/LLP 99.0/1.0 by wt%, and (d) PLA/LLP 98.0/2.0 by wt%.

The surface property of the pristine PLA coated glass substrate showed smooth surface morphology (Fig. 2a). This is due to the soft nature of the PLA bio-polymer. Similarly, the PLA composite films prepared on the glass substrate by the use of LLP also showed smooth surface morphology due to the homogeneous mixing. The LLP were deposited at the center of the layers of PLA film (Fig. 2b). On the other hand, the surface morphology of the PLA/LLP composite films showed the formation of hierarchical particles on the surface while increasing the LLP content (Figs. 2c and 2d). The images of Figs. 2c and 2d clearly showed the LLP content in the PLA/LLP films are responsible to enhance the surface contact angle. However, melting behaviors of composites and PLA were almost similar. This indicates that a crystallinity of composites was unchanged by adding LLP due to small LLP content in the composite.

The smooth surface of pristine PLA film became porous structures by enzymatic degradation at pH 8.5 in 37.5°C. The change in the surface morphology of the film was checked at 72 h of enzymatic degradation (Fig. 3a). Similarly, the PLA/LLP composite film (P99.4) also produces the porous structures on the surface (Figs. 3b-3d). The porous structures developed on the smooth surface might be due to the enzymatic degradation of PLA. On the other hand, the PLA/LLP composite film (P99.4) showed almost similar surface morphology to the pristine PLA after enzymatic degradation (Fig. 3b). Sample P99 and P98 showed quite reduced porous structure of the smooth PLA film as compared with the pristine PLA and sample P99.4 (Figs. 3c and 3d)) even at 72 h of degradation. The significant changes in the surface property were due to the reduced surface degradation of the films by enhanced hydrophobicity. The obtained results indicate that the LLP content is playing a crucial role for the enzymatic degradation of PLA. Consequently, the degradation rate of the PLA/LLP composite films was controlled by increasing the amount of LLP content.

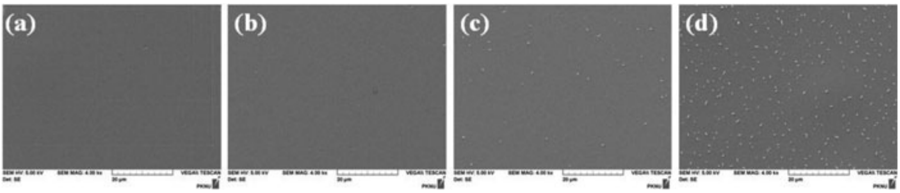

Figure 2. SEM images of pristine PLA and PLA/LLP composite films before enzymatic degradation. (a) pristine PLA, (b) PLA/LLP 99.4/0.6 by wt%, (c) PLA/LLP 99.0/1.0 by wt%, and (d) PLA/LLP 98.0/2.0 by wt%.

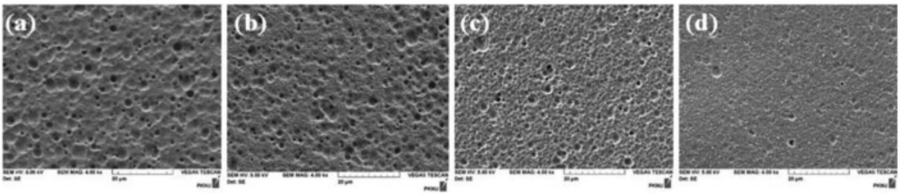

Figure 3. SEM images of pristine PLA and PLA/LLP composite films after 72 h enzymatic degradation. (a) pristine PLA, (b) PLA/LLP 99.4/0.6wt%, (c) PLA/LLP 99.0/1.0 wt%, and (d) PLA/LLP 98.0/2.0 wt%.

Summary

In this work, we fabricated hydrophilic and hydrophobic PLA films by simple modification of the amount of LLP contents at fixed amount of PLA under casting method. The surface property of the PLA/LLP composite films was changed by increasing the LLP content. The pristine PLA and PLA/LLP composite films showed smooth surface morphology at lower LLP content and hierarchical particles were developed on the surface at higher LLP content. The surface properties of the pristine PLA and PLA/LLP composite films were changed to porous structures by enzymatic degradation. The obtained preliminary results highlight that the degradation rate of the PLA/LLP composite films were controlled by increasing the LLP content due to the hydrophobic effect.

Acknowledgments

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