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A Useful Biomass Component for Simple Fabrication of the Honeycomb Poly(L-lactide) Film

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This concept is the development of useful material based on biomass such as a poly(L--lactide) [PLLA] with new added-value to extend applications. PLLA, which is an attractive raw material produced from renewable resources, has received much attention for applications in bioabsorbable and biodegradable materials. However, PLLA is not utilized well for practical use. This paper has explored an additive compound, which is a biocompatible, to facilitate a regular patterned porous film from PLLA to provide a valuable material. The method we adopted was to form a regular pattern on polymer film containing a surfactant in order to help the amphiphilic polymer to migrate at the interface between the organic solvent and the water droplets as the water-assisted formation method. To give the regular patterned porous film, some compounds from biomass were used for the water-assisted formation method. As surfactants in PLLA solutions, the experimental results showed the effectiveness of soy-bean oil. The pore size and surface morphology on the film can be controlled through the moisture condition, the PLLA concentration, and the molecular weight of PLLA.

Many researchers have focused on the development and use of biomass material for achieving a sustainable society. One of sustainable biomass materials is poly(L-lactide)[PLLA] which made from starch or cellulose in biomass, has received much attention for applications in bioabsorbable and biodegradable materials.[1-3] This polymerization and depolymerization behavior is one of the special properties of PLLA and it is very important for polymer science and technology supporting a green sustainable society.[4] However, in practical applications, PLLA does have some drawbacks, such as low thermal property, low impact resistance, and hydrolyzability. Applications of PLLA are not optimal to use widespread, it is difficult to substitute from application of fossil fuel based plastics. Therefore, other strategies for the effective use of PLLA are required. A fundamental and complete solution to this problem requires a design of the valuable materials to provide new applications.

The preparation of ordered polymeric films by the self-organization is an attractive field of researches due to its potential applications in the area of nano- and microtechnology. The use of honeycomb porous films is attractive in the high technology applications such as optic and optoelectronic devices [5] as well as cell growth scaffold for tissue engineering.[6] Many strategies are currently investigated to control the structure, the dimensions, and the regularity of the patterns that can be obtained. François et al. gave the honeycomb porous films using the self-organization of polystyrene polymer which is known as 'breath figures' method or water droplets template method.[7] This simple and efficient method has been used and applied to a wide range of polystyrene and other synthetic polymers.[8] Some materials from biomass such as poly(lactide-co-glycolide)[9,10], and poly(lactide)[11-13] notably has also been used for biomedical applications. The microporous films can be obtained when a spread polymer solution is evaporated on a substrate under its proper conditions such a humid atmosphere. In situ observation of the film formation process revealed that microspheres of water were formed by the condensation of atmospheric water at the interface between air and polymer solution.[14] The water-assisted formation method usually needs some surfactant in order to help the amphiphilic polymer to migrate at the interface between the organic solvent and the water droplets.

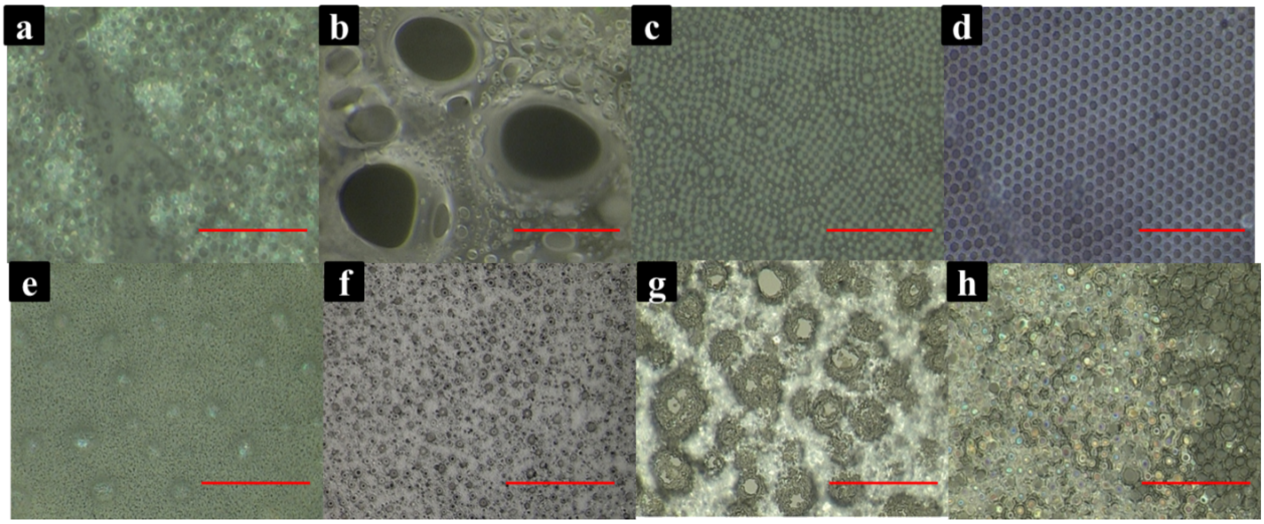

Figure 1. Microscope images of honeycomb film was construct from PLLA with additive from biomass, no additive (a), lactic acid (b), Lecithin from egg (c), Lecithin from soybean (d), Lauric acid (e), Palmatic acid (f), Lauramide acid (g), Ricinoleic acid (h), as PLLA: additive ratio (×5000, Bar = 50μm).

Since PLLA has good biodegradability and biocompatible, the porous PLLA films with honeycomb structures can be used as biomaterials, such as cell culture substrates or adhesion inhibitors for preventing postoperative adhesion. Qin et al. has fabricated a honeycomb structure films comprising commercial polymers, including polystyrene (PS), polycarbonate (PC), polylactic acid (PLA), and polymethylmethacrylate (PMMA) in $CHCl_3$ via breath figures method.[15] However, amphiphilic molecules must be prepared by using organic or polymer synthesis techniques corresponding to wettability control between polymer and water to form honeycomb structure films comprising poly(L-lactide) in solvent. On the other hand, Li et al. proposes to use PLLA dissolved in tetrahydrofuran (THF) in order to produce honeycomb film without surfactant.[16] Since the ordered array of the stabilised droplets is obtained under the interaction between the droplets and the convection in the polymer solution, their porous films were restrictively obtained by the formation process of droplets under certain conditions.

Our concept establishes a simple fabrication technique of the functional surface with PLLA as bio-based material. The origin of functional materials in nature is attributed to the presence of highly structured or ordered arrangements. The simple fabrication method for honeycomb film of PLLA prefers to use biomass-based additive for the biocompatible and biodegradability applications. However, surfactants derived from biomass have rarely been reported on the water-assisted method. We explored an additive compound, which is biocompatible, to conveniently make regular patterned porous film from PLLA. In this report, we show that regular porous films were successfully obtained by PLLA with additive of biomass-based surfactant.

The feasibility of this method for the preparation of various porous structures will be demonstrated by using seven different kinds of biomass-based materials such as lactic acid, laulic acid, palmitic acid, lauramide acid, recinoleic acid, lecithin from egg, lecithin from bean, either with or without surfactant. In our study, many additives were selected for construction of the porous film. Fig. 1 shows microscope images of porous films fabricated by direct casting 1.5 mL of PLLA (Mw 110,000) and an additive substance (10:1) solution (4.0 mg/mL) in chloroform onto the Petri dish (diameter 5.2 cm) under a moist N_2 flow. After casting, moist nitrogen gas (relative humidity, 75% at 25ºC) was blown vertically onto the solution (gas-flow rate 3.0 L/min). The prepared film was observed by the optical microscope and the scanning electron microscopy (SEM, S-3500N, HITACHI, Japan) after complete evaporation of the solvent and the condensed water.

Thin-layer of PLLA films with an additive were prepared by the self-organization of matter. However, the resulting of some products was disordered porous morphology. The additives don't work as surfactants due to the miscibility in water in the water-assisted method, they were not beneficial except for the lecithin from soybeans to stabilise the templates. Without additive, it has not been possible to produce honeycomb film. Some porosity is observable but the pores size and the layout are not regular. Interestingly, the porous regularly patterned film was only produced with the lecithin from soybean, but not produced with the lecithin from egg as shown in Fig. 1c-d. The lecithin made from soybean, which is commercially available, demonstrated the high additive effect to fabricate the regular porous honeycomb shaped film (Figure 2). And also, the micro-scale pores on the resulting film showed the same pore size and regularly aline.

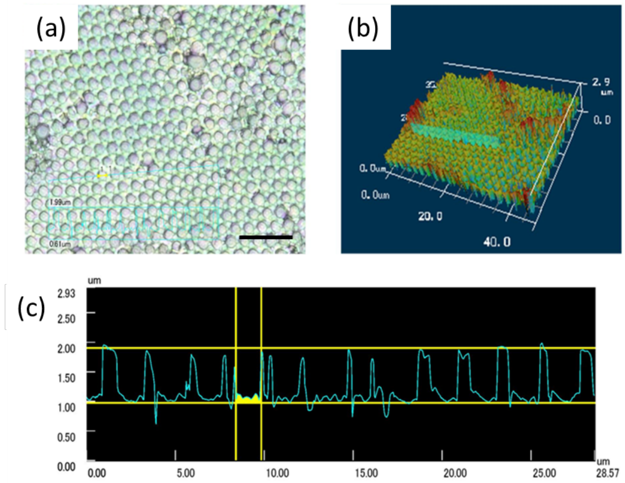

Figure 2. Digital images of the honeycomb film with soybean oil, a) microscope image(Bar= 10μm), b) 3D image, c) cross-section profile.

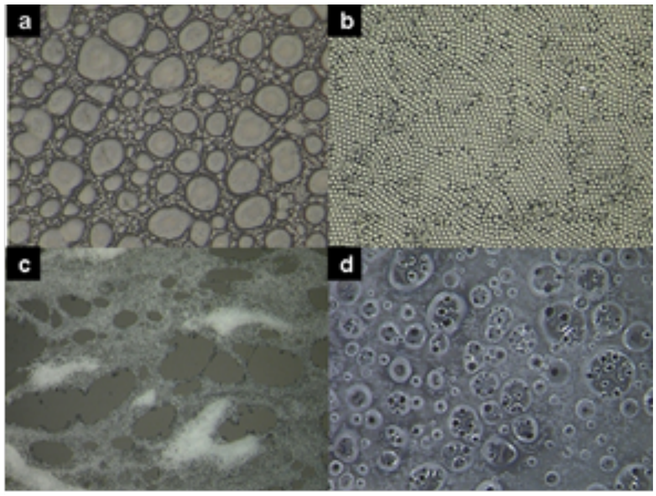

Figure 3. Microscope images of PLLA film by using various solvents a) dichloromethane b) chloroform c) acetonitrile d) THF (×1000).

In contrast, lecithin from egg mainly contains phosphatidyl choline and phosphatidyl ethanolamine. And also lecithin in soybeans contains higher concentration of total unsaturated fatty acids than that in egg. [18] It means that lecithin from soybeans has different components compared with egg, and it's complicate components.

The control of porous PLLA film using lecithin extracted from soybean is as yet inadequately known and needs further investigation even though some factors for the preparation of porous film are currently under consideration. In the beginning, the influences of the solvent on regular pattern formation might need to be taken into consideration. In order to study the influences of the solvent on the formation of honeycomb structures, the PLLA with lecithin were respectively dissolved in four kinds of solvent and to attempt the formation of porous film. These solvents were acetonitrile, chloroform, dichloromethane, and THF (Figure 3). The solvent effect on the morphology was investigated by the mixture of PLLA (4.0 mg/mL) with the lecithin from soybean in various solvent. PLLA film with lecithin was dissolved in these solvents and formed membranes under a high-moist atmosphere. Generally, inadequate solvent to stabilise water droplet such as water-miscible solvents was not employed in the water assisted method due to their miscibility in water. PLLA films with porous structures were not obtained by evaporating the PLLA including lecithin in MeCN under humid conditions. By evaporating PLLA solution in $CHCl_3$ or CH_2Cl_2 as water-immiscible solvents, porous PLLA films were obtained under humid conditions. However, the CH_2Cl_2 was faster evaporated from PLLA solution, the resulting product showed the irregular and larger porous film obtained. And the disordered porous PLLA film was obtained when the water miscible solvent such as THF were utilised. Certainly, $CHCl_3$ is well known to show the good solubility for the PLLA. The volatility of the solvent could not only influence the pore sizes of the honeycomb film, but also determined whether or not the regular porous structure could be achieved to condense on the surface of the solution. It is supposed that water droplets were maintaining the shape at the interface between the two phases due to appropriate for volatility and solubility of the solvent for the preventing from aggregation of the water droplets, and thereby giving rise to the regular structures. However, other influences of the solvent on regular pattern formation might need to be taken into consideration.

Conclusions

In summary we have demonstrated the usefulness of lecithin made from soybean as a new additive based on biomass for the water-assisted method to fabricate the regular porous and honeycomb shaped PLLA film. This conceptually new and simple method has allowed the formation of highly uniform PLLA porous film. In addition, the porous PLLA film including the lecithin is not included except biomass derivatives and can be used in biomedical fields because of its biocompatible and biodegradability. This novel approach might be expanded to allow the preparation of the various micro, nano-area template structures, which expect to collaborate with metallic, inorganic, biological and polymeric materials. Further consideration will be needed to reveal the usefulness of lecithin for the preparation of the regular porous film from various materials.

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