Highly ordered porous PLA films prepared by breath figure method

Charasphat PREUKSARATTANAWUT[1,*], Ekkasit NISARATANAPORN[1], and Krisana SIRALERTMUKUL[2,*]

[1] *Innovative Metal Research Unit, Department of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai road, Wangmai, Phathumwan, Bangkok, 10330, Thailand*

[2] *Metallurgy and Materials Science Research Institute, Chulalongkorn University, Soi Chula 12, Phayathai road, Wangmai, Phathumwan, Bangkok, 10330, Thailand*

*Corresponding author e-mail: krisana.s@chula.ac.th

Abstract

Honeycomb-patterned porous biodegradable PLA film can be successfully prepared by the Breath Figure (BF) method, which is a self-assembly template and low-cost process. In this research, the fabrication was designed to create a convenient and simple process aimed at meeting commercial requirements. Production of regularly ordered pattern microporous film is carried out in a closed system with optimum conditions. Thus, important production factors —that is, the starting polymer concentration in solution, the type of solvent (which affects the solvent evaporation rate), and the relative humidity of the closed chamber —were investigated to identify the optimum conditions. The results showed that highly ordered porous film with smaller average pore size of 23.29±4.55 µm on strut was generated (19.98±2.82 µm) when high PLA concentration (10% wt PLA) in dichloromethane with 80-85% RH relative humidity was applied.

1. Introduction

Recently, microporous polymer film has been widely used in many applications such as electronic techniques [1], biotechnologies [2] and more due to its pore dimensions, high specific surface area, and high oxidation resistance. However, using large quantities of traditional polymer in daily life exacerbates the global waste crisis the world now faces Biodegradable polymeric materials are one of the best alternative solutions.

The Breath Figure (BF) method is a convenient and simple technique that requires only the evaporation of a solvent and condensation of water vapor in a controlled atmosphere. The evaporation of the solvent surface generates a thermal gradient between the atmospheric temperature and the solvent surface temperature due to endothermic reaction. The water vapor is condensed into water droplets, overspreading the surface of the polymer solution. When the solvent and the water droplets evaporate completely, a honeycombed patterned or spherical-shaped array of pores is formed in the solid polymer surface [3-5]. In using this technique, various factors play important roles in controlling the porous polymer structure, including polymer concentration, type of organic solvent used, and humidity [6-8]. Several applications of synthetic porous polymer thin films fabricated from BF technique have been applied in separation or filtration [9], sensing technology [10], and drug delivery [11], as well as in cell scaffolding in tissue engineering [12].

Nowadays, the self-template technique for producing microporous polymer film has become more popular due to cost reductions achieved on both the template and by removing steps. The Breath figures (BF) method, known as an alternative approach that offers a fast-growing, self-template technique to effortlessly prepare micro-sized honeycomb highly-ordered porous films, is quite remarkable [13,14]. Interesting bioplastics especially poly (lactic acid) or PLA, synthesized from lactic acid can be produced from renewable natural resources such as corn, sugarcane, cassava, and other agricultural wastes. Owing to its specific properties, PLA can replace conventional synthetic plastics, providing benefits due to its biodegradability, bio-compatibility, and high thermo-mechanical property. At present, PLA is mainly used in packaging products and biomedical applications [15-17]. Previous research has attempted to fabricate ordered porous PLA films by using a solvent casting, along with a phase-separation technique [18,19]. Nevertheless, only the method of PLA, blended with the process of combining two or more self-assembly molecules, can be used to successfully produce a honeycomb microporous structure [20]. Thus, the process of porous PLA films using by BF technique, which is a simple, rapid and environmental friendly technique for preparation of highly-ordered porous film, offers a very promising research opportunity. The effect of important parameters on film production, including PLA concentration, organic solvent, and relative humidity, is investigated in this study.

2. Experimental

2.1 Materials

Poly (lactic acid) 4043D (M_w = 1.5X105 g·mol^{-1}, and molar-mass dispersity, Đ=1.81) Nature Works,

US was used for PLA microporous film preparation. Dichloromethane and Chloroform, Aldrich, Germany were used as the solvents. Other chemicals used in this work were reagent grade.

2.2 A microporous film preparation

The solution of PLA in dichloromethane or chloroform at various concentrations of 1.5%, 3%, 5%, and 10%, respectively, were prepared, and then each polymer solution was further cast onto a petri dish under controlled humidity inside of a closed chamber. The relative humidity [RH] was controlled in two ranges of 58-65% and of 80-85%RH using an aqueous solution of sodium chloride, and measured by means of hygrothermograph. In order to investigate the effects of 3 factors; (1) PLA concentration, (2) organic solvent (dichloromethane and chloroform) and (3) relative humidity, were studied in this research. After the solvent had been completely evaporated, PLA porous films were successfully formed. The obtained film surface morphologies were analyzed using Scanning Electron Microscopy (JEOL, Model JSM-6400, Japan), the pore size was measured by Axio Vision Rel. 4.8 software, and BET measurement was carried out using a Quantachrome Autosorb iQ Station 1 at 77.35 K. The sample was degassed under vacuum at 30°C for 16 h prior to measurement.

3. Results and discussion

A series of microporous PLA films ranging in thickness from 50 to 80 microns was prepared and all the effects of the experimental parameters were investigated.

3.1 PLA concentration

Figure 1 shows the surface morphologies of porous films which were analyzed by SEM. It can be clearly seen that all films which were prepared by the BF method with dichloromethane at 80-85%RH and variations of the concentration between 1.5-10%wt. exhibit honeycombed ordered single porous structure on the top of each film. When the polymer solution was cast on the substrate in the closed system, the solvent evaporation resulted in a droplet, and the surface temperature of the solution was below the Dew point temperature. The decrease in temperature led to the condensation of water droplets on the top of solution, and, thus, the droplets sank into the surface solution, whereas the viscosity of the solution gradually increased owing to the vaporization. This finally led to creation of pores on the surface. Furthermore, during the process of increasing viscosity, the condensation of water droplets on the solution stabilized, and their flow ability decreased and prevented them from coalescing or aggregating [21]. To elaborate, as shown in Figure 1g and 1h, the average size of core pores was getting smaller, from 23.97±4.14 µm to 19.98±2.82 µm, as the concentration increased from 5% to 10%wt. Simultaneously, the average size of small pores between the cell wall of core pores was also getting smaller (in the pore size range from 12.44-34.67 µm to 11.05-29.11 µm) and creating more ordered patterns with narrow pore size distribution (Table 1). This can be explained by the fact that increasing viscosity over the process time decreased the flow ability and inhibited the coalescence of small pores; thus, a number of smaller average sized core pores appeared. Another factor is that, at the higher degree of concentration, initial vapor pressure of solvent decreased compared to that of the lower degree, and, as the process time went by, the remaining solvent continuously vaporized, condensing into droplets and forming pores on the cell wall of the core pores. At the higher concentration, there was more remaining volume of solvent than at the lower concentration. The solvent still evaporated through the core pore to the top surface. When there was enough vapor pressure, the vapor condensed into water droplets and sank into the cell wall of core pores during solidification process. More time was needed for the condensation to occur, and so the droplets did sink, which resulted in more and more small pores on the cell wall of core pores [22]. With the higher concentration of PLA polymer, films with a more ordered pattern with smaller and more uniform pores were obtained. This resulted from an increase in the initial viscosity level of higher concentrated solution when compared with the lower concentration.

Table 1. Average pore size and pore size range of PLA microporous film at different PLA concentrations (%) and dried at 80-85%RH.

PLA concentration(%wt.)	Average pore size (µm)	Pore size range (µm)
1.5	25.96±7.13	13.03 - 50.66
3	23.22±4.10	12.58 - 36.60
5	23.97±4.14	12.44 - 34.67
10	19.98±2.82	11.05 - 29.11
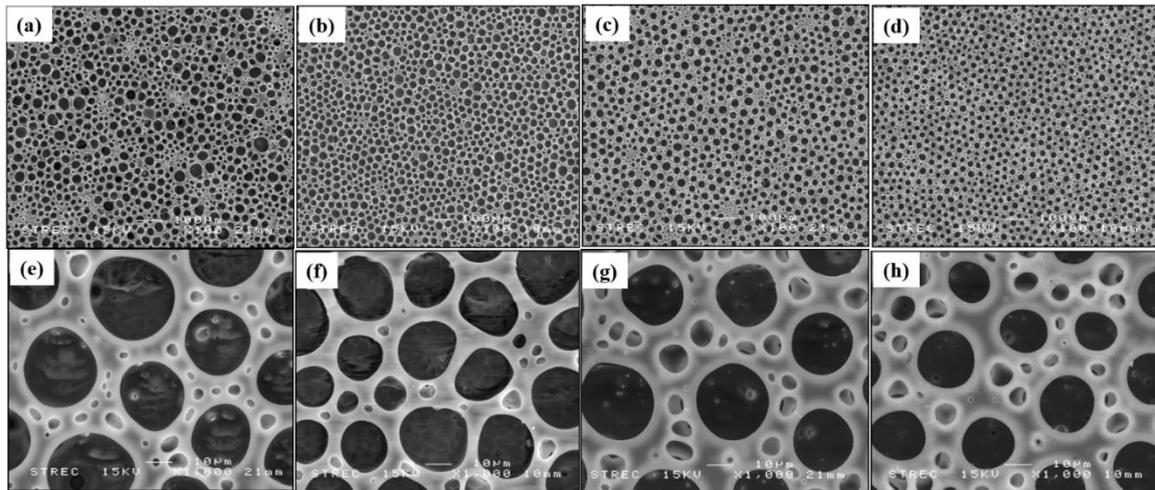
Figure 1. SEM images at 100X and 1,000X magnification of the PLA film preparation by BF method with different PLA concentrations: (a), (e) 1.5%PLA, (b), (f) 3%, (c), (g) 5% and (d), (h) 10% of dichloromethane used as solvent at >80-85%RH.

3.2 Organic solvents

The influence of different types of solvent on the final surface microstructure of the single honeycomb porous layer of film is illustrated in Figure 2. The results show that both dichloromethane and chloroform can successfully be used to form porous films with honeycomb ordered patterns. However, the dichloromethane-added films produced a much more ordered pattern with smaller pores than did the chloroform-added films. This resulted from the differences in boiling points of the two solvents. From Table 2, Dichloromethane (dielectric constant of 4.81 and 61 B.P.) can be used as a substitute for Chloroform (dielectric constant of 8.93 and 40 B.P.). As a solvent, Chloroform is more popular and less expensive but more toxic than dichloromethane. Dichloromethane has a higher dielectric constant, which means it is more polar than chloroform and has a lower boiling point; therefore, Dichloromethane evaporates faster and creates higher vapor pressure on the top surface solution than does Chloroform. In other words, the porous film prepared with dichloromethane had more driving force to nucleate the condensed water droplets on the solution surface. The larger number of droplets were dispersedly formed on the surface as the solvent evaporated. The viscosity of the solution increased while the solvent evaporated. Using Chloroform, with its associated lower vapor pressure, the condensation of water vapor was slower and took more time to evaporate. The level of viscosity of the solution with chloroform as solvent increased at a slower rate than that of the solution using dichloromethane. Thus, this allowed the water droplets to flow and coalesce more feasibly, and to form bigger pores, which is why the obtained film from dichloromethane showed more ordered and smaller pore size.
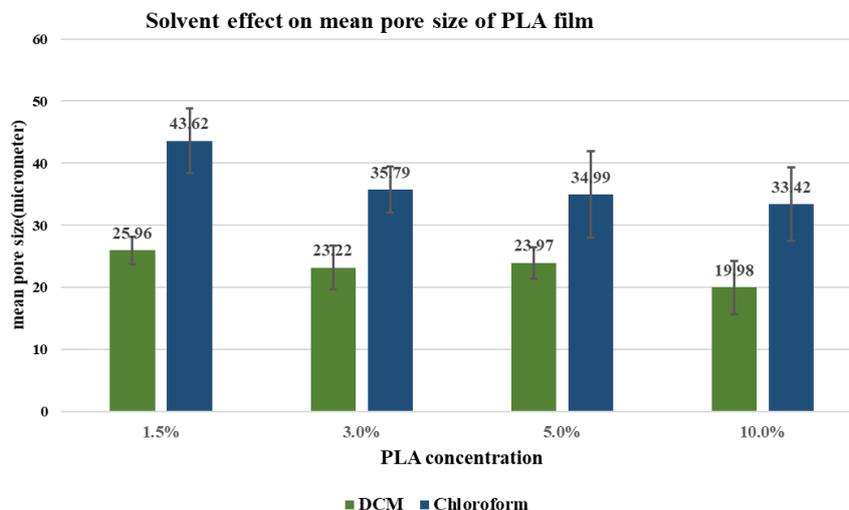
Figure 2. Revealed effect of Dichloromethane and Chloroform as solvents on the pore size of porous PLA films obtained from 1.5%, 3%, 5%, and 10% PLA respectively at >80-85%RH.

Table 2. Physical properties of solvents.

Property	Dichloromethane	Chloroform
Formula	CH_2Cl_2	$CHCl_3$
Boiling point (°C)	39.6	61.2
Density (g·cm^{-3})	1.33	1.498
Surface tension (dyn·cm^{-1})	28.12	27.16
Vapor pressure 20°C (hPa)	470	210
Dielectric constant	9.08	4.81

3.3 Relative humidity (%RH)

As can be seen from the results shown in Figure 3 and Figure 4, with 3% and 5% PLA polymer film, the relative humidity (RH) of 58-65% was insufficient to produce an ordered pore morphology. Moreover, the small amount of PLA solution (3% and 5%) provided viscosity that was too low to stabilize the water droplets sinking into the surface as the solvent evaporation is very fast, causing the water vapor to rapidly condense on the surface [23]. It is this non-equilibrium state that leads to the so-called vanishing of some parts of pore structure on the surface.

When the PLA concentration was increased to 10%, highly ordered spherical shapes on the surface of the obtained film were clearly observed. The higher concentration of polymer in volatile solvent causes the solute to precipitate out of the solution faster, and increase the viscosity of the solution as the solvent evaporates than is true with the lower concentration

[24]. The increased viscosity of the 10% solution was sufficient to stabilize and improve the ability of encapsulation the condensed water droplets. This phenomenon can keep the water droplet in the solution until the solidification is perfectly completed. Thus, using the higher PLA concentration of 10% leads to production of the obtained film with a honeycomb ordered pattern at 58-65%RH.

When of 80-85% RH was used to fabricated the polymer films, PLA porous films with highly ordered porous structure was able to be formed using all of the tested PLA solutions (3%, 5%, and 10%). At higher %RH, there is more driving force to condense the water droplets than at lower relative humidity. The greater the amount of water droplets generated on the surface, the greater the possibility of fabrication of pores on the surface; thus, ordered porous structure films can be produced with a low concentration of PLA (3%).

Dichloromethane as solvent

Chloroform as solvent
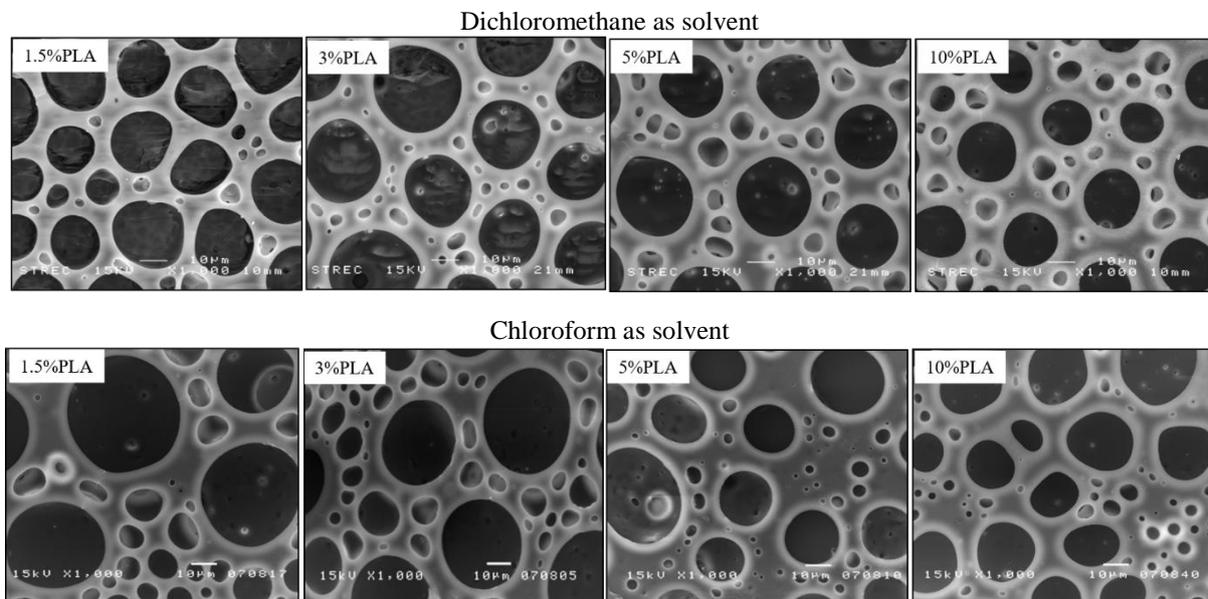
Figure 3. Revealed effect of Dichloromethane and Chloroform as solvents on the pore size of porous PLA films obtained from 1.5%, 3%, 5%, and 10% PLA respectively at >80-85%RH analyzed by SEM images at 1,000X.
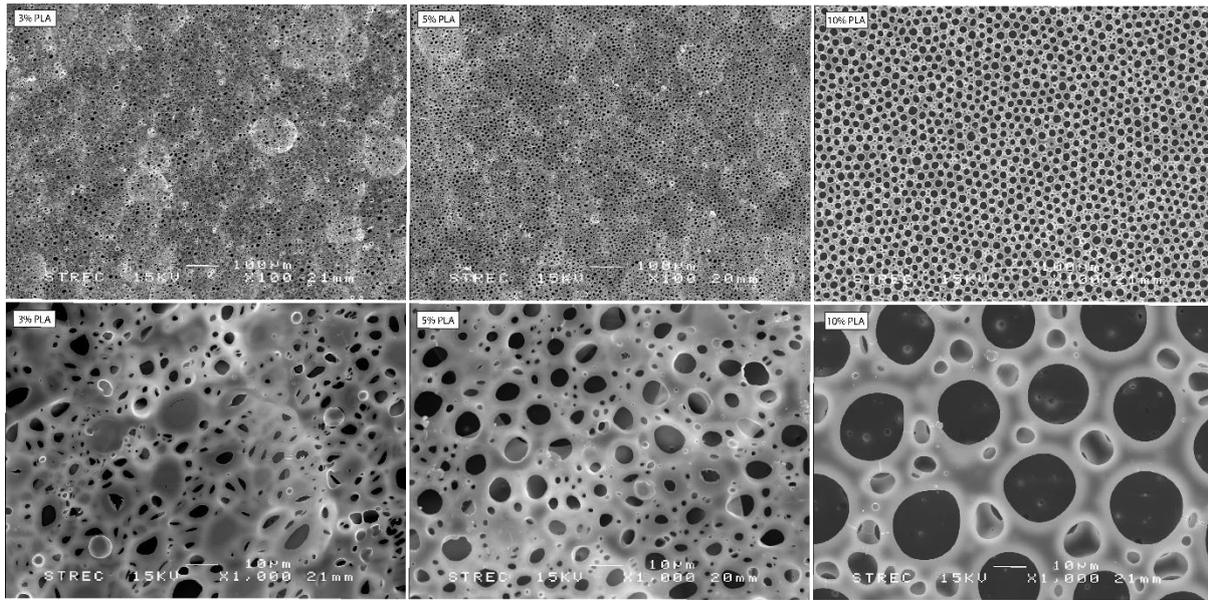
Figures 4. SEM images at 100X and 1,000X magnification of the PLA films preparation by BF method with different PLA concentrations by using dichloromethane as solvent at >58-65%RH.

At high relative humidity, many water droplets condense onto the surface solution, unavoidably affecting the growth and coalescence of some water droplets. The results of increasing concentration and %RH is that pore size increased. However, at 10%PLA, both RH values led to exactly the same average pore size of 21.07 ± 2.43 and 19.98 ± 2.82 µm for 58-65% RH and 80-85%RH respectively (Table 3). The porous film at 10%PLA had already reached equilibrium at 58-65%RH, so even an increase in RH will not affect the increase in pore size afterwards. However, an important parameter to be considered is the surface area of the microporous PLA film as shown in Table 4. When high relative humidity (80-85%RH) was used, the surface area of PLA films tended to increase due to the increase in water condensation on the surface; pore sizes become larger and higher in surface area in this case. The surface area of samples decreases when PLA concentration was increased.

Table 3. The effect of %RH on an average pore size and pore size range of PLA films.

PLA concentration	Average pore size (µm)	Pore size range (µm)
RH 58-65%		
3%PLA	6.35 ± 2.22	2.37 - 14.32
5%PLA	6.67 ± 1.65	3.02 – 10.91
10%PLA	21.07 ± 2.43	13.42 - 30.55
RH 80-85%		
3%PLA	23.22 ± 4.10	12.58 - 36.60
5%PLA	23.97 ± 4.14	12.44 - 34.67
10%PLA	19.98 ± 2.82	11.05 - 29.11

Table 4. PLA film surface area at various RH conditions and concentrations.

PLA concentration (%wt)	Surface area ($m^2 \cdot g^{-1}$)		Pore volume ($ml \cdot g^{-1}$)	
	Low RH (58-65%)	High RH (80-85%)	Low RH (58-65%)	High RH (80-85%)
3	92.15	182.40	0.134	0.30
5	49.46	113.90	0.056	0.12
10	38.14	99.72	0.052	0.10

4. Conclusions

Highly ordered porous PLA films were successfully fabricated in dichloromethane and chloroform by BF method. The results show that an increase in polymer concentration leads to decrease in the average pore size of porous polymer films. Thus understanding polymer soluble in organic solvent with different boiling points, density, and solubility properties and dielectric constants can help explain the mechanism of porous formation during the evaporation of solvent and water. Also, an increase in relative humidity creates more highly ordered porous PLA films with the larger pore size. Ultimately, the highest surface area in porous structure was obtained with 3%PLA in dichloromethane and 80-85% relative humidity.

5. Acknowledgements

References

[1] E. Menard, M. A. Meitl, Y. Sun, J. U. Park, D J. L. Shir, Y. S. Nam, S. Jeon, and J. A. Rogers, "Micro- and Nanopatterning Techniques for Organic Electronic and Optoelectronic Systems," *Chemical Reviews*, vol. 107, no. 4, pp. 1117-1160

[2] T. Nishikawa, M. Nonomura, K. Arai, Junko Hayashi, T. Sawadaishi, Y. Nishiura, M. Hara, and M. Shimomura, "Micropatterns Based on Deformation of a Viscoelastic Honeycomb Mesh," *Langmuir*, vol. 19, no. 15, pp. 6193-6201

[3] D. Maniglio, Y. Ding, L. Wang, and C. Migliaresi, "One-step process to create porous structures in cross-linked polymer films via breath-figure formations during in situ cross-linking reactions," *Polymer*, vol. 52, no. 22, pp. 5102-5106

[4] L. Li, Y. Zhong, J. Li, J. Gong, Y. Ben, J. Xu, X. Chen, and Z. Ma, "Breath figure lithography: A facile and versatile method for micropatterning," *Journal of Colloid and Interface Science*, vol. 342, no. 1, pp. 192-197, 2010/02/01.

[5] J. S. Arora, T. Ponnusamy, R. Zheng, P. Venkataraman, S. R. Raghavan, D. Blakec, and V. T. John, *Spatially Directed Vesicle Capture in the Ordered Pores of Breath-Figure Polymer Films*. 2015.

[6] J. Peng, Y. Han, Y. Yang, and B. Li, "The influencing factors on the macroporous formation in polymer films by water droplet templating," *Polymer*, vol. 45, no. 2, pp. 447-452, 2004/01/01.

[7] R. Zhang, J. Wang, M. Wang, and Y. He, "Fabrication of honeycomb polyvinyl butyral film under humidity provided by super

saturated salt solutions," *Journal of Applied Polymer Science*, Article vol. 124, no. 1, pp. 495-500, 2012.

[8] C.-X. Liu, W.-Z. Lang, B.-B. Shi, and Y.-J. Guo, "Fabrication of ordered honeycomb porous polyvinyl chloride (PVC) films by breath figures method," *Materials Letters*, vol. 107, pp. 53-55, 2013/09/15.

[9] H. Yuan, B. Yu, H. Cong, Q. Peng, Z. Yang, Y. Luo, and M. Chi, "Preparation of highly permeable BPPO microfiltration membrane with binary porous structures on a colloidal crystal substrate by the breath figure method," *Journal of Colloid and Interface Science*, vol. 461, pp. 232-238, 2016/01/01.

[10] S. Miller and Z. Bao, "Fabrication of flexible pressure sensors with microstructured poly-dimethylsiloxane dielectrics using the breath figures method," *Journal of Materials Research*, vol. 30, no. 23, pp. 3584-3594, 2015.

[11] K. Kummerer, "Sustainable from the very beginning: rational design of molecules by life cycle engineering as an important approach for green pharmacy and green chemistry," *Green Chemistry*, vol. 9, pp. 899-907, 2007.

[12] H. Itoh, Y. Aso, M. Furuse, Y. Noishiki, and T. Miyata, *A honeycomb collagen carrier for cell culture as a tissue engineering scaffold*. 2001, pp. 213-7.

[13] Y. Hiroshi, "Fabrication of honeycomb films by the breath figure technique and their applications," *Engineering and Structural Materials*, vol. 19, No. 1, pp. 802-822, 2018.

[14] A. Zhang, B. Hua, and L. li, *Breath Figure: A Nature-Inspired Preparation Method for Ordered Porous Films*. 2015.

[15] S. Farah, D. G. Anderson, and R. Langer, "Physical and mechanical properties of PLA, and their functions in widespread applications — A comprehensive review," *Advanced Drug Delivery Reviews*, vol. 107, pp. 367-392, 2016/12/15.

[16] J.-M. Raquez, Y. Habibi, M. Murariu, and P. Dubois, "Polylactide (PLA)-based nano-composites," *Progress in Polymer Science*, vol. 38, no. 10, pp. 1504-1542, 2013/10/01.

[17] R. Auras, B. Harte, and S. Selke, "An Overview of Polylactides as Packaging Materials" *Macromol. Biosci*, vol. 4, pp. 835–864 2004

[18] Q. Cai, J. Yang, J. Bei, and S. Wang, "A novel porous cells scaffold made of polylactide–dextran blend by combining phase-separation and particle-leaching techniques," *Biomaterials*, vol. 23, no. 23, pp. 4483-4492, 2002/12/01.

[19] T. Phaechamud and S. Chitrattha, "Pore formation mechanism of porous poly(dl-lactic acid) matrix membrane," *Materials Science and Engineering: C*, vol. 61, pp. 744-752, 2016/04/01

[20] Y. Andou, S. Pattanawihok, V. Jauzein, M. Wakisaka, Y. Shirai, and H. Nishida, "a useful

PREUKSARATTANAWUT, C., et al.

biomass component for simple fabrication of the honeycomb Poly(L-lactide) Film," *Nanobio Bionano* 2014.

[21] E. Bormashenko, A. Musin, Y. Bormashenko, G. Whyman, R. Pogreb, and O. Gendelman, "Formation of films on water droplets floating on a polymer solution surface," *Macromolecular Chemistry and Physics*, Article vol. 208, no. 7, pp. 702-709, 2007.

[22] B. Guerrier, C. Bouchard, C. Allain, and C. Bénard, "Drying Kinetics of Polymer Films," *AIChE Journal*, Article vol. 44, no. 4, pp. 791-798, 1998.

[23] X. Xiong, M. Lin, W. Zou, and X. Liu, "Kinetic control of preparing honeycomb patterned porous film by the method of breath figure," *Reactive and Functional Polymers*, vol. 71, no. 9, pp. 964-971, 2011/09/01.

[24] M. Huh, M.-H. Jung, Y. S. Park, T.-B. Kang, C. Nah, R. A. Russell, P. J. Holden, and S. I. Yun, "Fabrication of honeycomb-structured porous films from poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) via the breath figures method," *Polymer Engineering & Science*, vol. 52, no. 4, pp. 920-926, 2012/04/01