

# Plasticization of Poly (lactic) acid Film as a Potential Coating Material

Ping Yang<sup>1,2</sup>, Hua Li<sup>1</sup>, Qingsong Liu<sup>1</sup>, Hongbiao Dong<sup>1</sup>, Yafei Duan<sup>1</sup> and Jiasong Zhang<sup>1,3,\*</sup>

<sup>1</sup>Key Lab of South China Sea Fishery Resources Exploitation & Utilization, Ministry of Agriculture South China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Guangzhou 510300, China

<sup>2</sup>National Demonstration Center for Experimental Fisheries Science Education, Shanghai Engineering Research Center of Aquaculture, Centre for Research on Environmental Ecology and Fish Nutrition (CREEFN) of the Ministry of Agriculture, Shanghai Ocean University, Shanghai 201306, China

<sup>3</sup>Shenzhen Base of South China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Shenzhen 518121, China

First author e-mail: yangping19588@163.com

\*Corresponding author e-mail: jiasongzhang@hotmail.com

**Abstract.** PLA-based composite films with different plasticizers, such as polyethylene glycol (PEG) and Tributyl citrate (TBC), were prepared using a solvent casting method and their mechanical, water absorbency and NO<sub>3</sub><sup>-</sup>-N permeability properties were tested. Tensile strength, elongation at break, water absorbency and NO<sub>3</sub><sup>-</sup>-N permeability of neat PLA film were  $1.99 \pm 0.04$  MPa,  $2.7 \pm 0.46\%$ ,  $29.33 \pm 0.3\%$  and  $216.03 \pm 19.92$  mg·L<sup>-1</sup>·m<sup>-2</sup>·h<sup>-1</sup>, respectively. After the addition of plasticizers the tensile strength were decreased, tensile strength of films added 40wt% TBC and PEG decreased by 59.3% and 52.26%. While the elongation at break of the PLA film gradually increased. The elongation at break reached the value of  $23.96 \pm 0.48\%$  and  $38.55 \pm 1.66\%$  for the films added PEG and TBC respectively at the concentration of 40wt%. Water absorbency decreased as the increase of plasticizers. The NO<sub>3</sub><sup>-</sup>-N permeability attained a maximum of  $300.05 \pm 10.47$  and  $270.97 \pm 14.54$  mg·L<sup>-1</sup>·m<sup>-2</sup>·h<sup>-1</sup> for films added PEG and TBC at the concentration of 10 wt % respectively. Considered the NO<sub>3</sub><sup>-</sup>-N permeability, PEG at 10wt% seemed the better plasticizer for PLA used in control release of fertilizer.

## 1. Introduction

The widespread contamination of surface and ground water quality from the heavy use of fertilizer in agriculture is the current concern[1,2]. To prevent further pollution, some film was used as coating materials to control release of fertilizer in agriculture[3]. Commonly used coating materials are sodium alginate (SA), polyvinyl alcohol (PVA) and poly (lactic) acid (PLA). PLA which was approved by the US Food and Drug Administration (FDA) as far back as the 1970s has since been widely utilized in the agricultural, industrial and medical industries[4]. It is widely used because it has good bio-



logical compatibility and significantly high strength and modulus. PLA's final products of degradation are CO<sub>2</sub> and H<sub>2</sub>O and the intermediate products are lactic acid and hydroxyl acid, which are harmless to the environment[5]. Despite its advantages, PLA is typically rigid and brittle, which significantly limits its application. In this article, PLA was plasticized with different concentration of PEG and TBC to overcome the drawbacks of low elongation, poor toughness and weak impact-resistance strength.

## 2. Materials and Methods

### 2.1. Materials

Poly (lactic) acid (PLA, 4032D) was purchased from the Nature Works. Chloroform (CHCl<sub>3</sub>) was obtained from Sinopharm Chemical Reagents Co., Ltd. China. Analytical grade poly ethylene glycol (PEG, average Mn400) and Tributyl Citrate (TBC) are purchased from Shanghai Macklin Biochemical Co., Ltd. China.

### 2.2. Preparation of PLA Film

PLA was first pre-drying in the vacuum drying oven at 80°C for 3h and then vacuum cooling. In a typical reaction 0.9 g PLA was first dissolved in 30mL chloroform to achieve a solution of 3% solid content. Next, PEG and TBC were added into the solution at the concentration of 10, 20, 30 and 40wt% respectively. The mixture was stirring with magnetic stirrer for 3h until it was completely dissolved. After releasing bubbles under room environment, the obtained casting solution was spread onto a glass plate. Finally, the glass was put into vacuum drying oven at 50°C for 4h, until the CHCl<sub>3</sub> had volatilizes then dye stripping the film off.

### 2.3. Mechanical properties

The universal mechanical testing machine INSTRON 3366 was used for the tensile test. Film were cut into 200×15 mm rec-tangle samples, and their effective tensile length was 150 mm. The uniaxial tensile test was carried out at a tensile rate of 5 mm/min. The average tensile strength and elongation was calculated from 3 samples. The measurements were performed in accordance with GB/T1040. The tests were performed with a pre-load force of 1 N.

### 2.4. Water Absorbency

Exactly weighed blend films (G<sub>1</sub>) were immersed in distilled water for 3h until sufficiently swollen. After took out from the water, the film blotted up the water on the surface was weighed (G<sub>2</sub>). The water absorbency was calculated by the equation of (G<sub>2</sub>-G<sub>1</sub>) /G<sub>1</sub>[6,7].

### 2.5. NO<sub>3</sub><sup>-</sup>-N Permeability

First, 50ml 50 mg/L NO<sub>3</sub><sup>-</sup>-N (NaNO<sub>3</sub>) solution was poured into the permeability cup sealed with the prepared film. Cup was put downwards in beakers containing 200 mL distilled water for 2h. The concentration of NO<sub>3</sub><sup>-</sup>-N in distilled water was determined using Thymol Spectrophotometry method. And the NO<sub>3</sub><sup>-</sup>-N permeability had been calculated by the formula

$$NP = \frac{DC}{tS}$$

Where NP is the NO<sub>3</sub><sup>-</sup>-N permeability(mg·L<sup>-1</sup>·m<sup>2</sup>·h<sup>-1</sup>), DC is the concentration of NO<sub>3</sub><sup>-</sup>-N in distilled water, t is the time, and S is the effective area of the film[6,8]

### 3. Results and Discussion

#### 3.1. Mechanical properties

The results of the tensile test are shown in Figure 1. The neat PLA was typically rigid and brittle. It had high tensile strength ( $1.99 \pm 0.04$  MPa), but with very limited elongation at break and the value is only  $2.7 \pm 0.46\%$  (Figure. 1b). After the addition of plasticizers, the tensile strength was decreased, tensile strength of the film added 40%wt TBC and PEG had a decrease about 59.3% and 52.26%. While the elongation at break of the PLA film gradually increased. This modification was more notable for the film with higher plasticizer concentration. The elongation at break reached the value of  $23.96 \pm 0.48\%$  and  $38.55 \pm 1.66\%$  for the films added PEG and TBC respectively at the concentration of 40wt%. These phenomena are as same as Lemmouchi, Chieng and Choi described [9-11]. According to theory, the plasticizer molecules may be totally immobilized by attachment to the polymer chains by various forces. Withal, plasticization causes a lower glass transition temperature ( $T_g$ ) of the polymer matrix leading to an increase in flexibility and ductility. This may be the reason for the enhancement of the elongation at break[12].

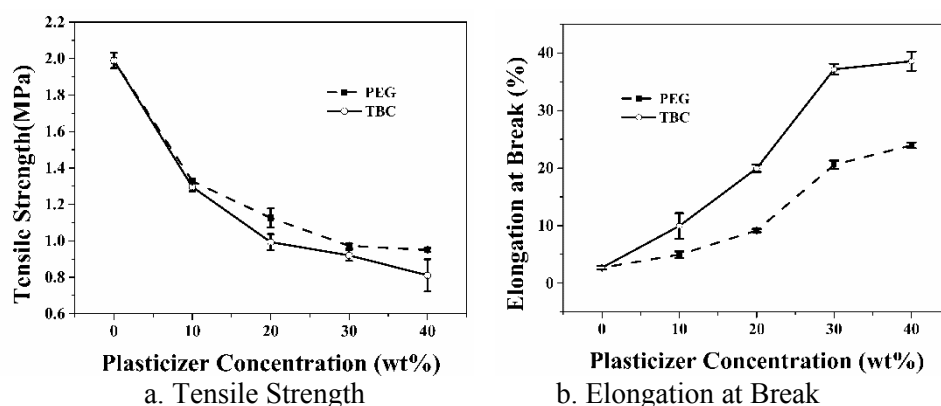


Figure 1. Mechanical properties of the PLA films

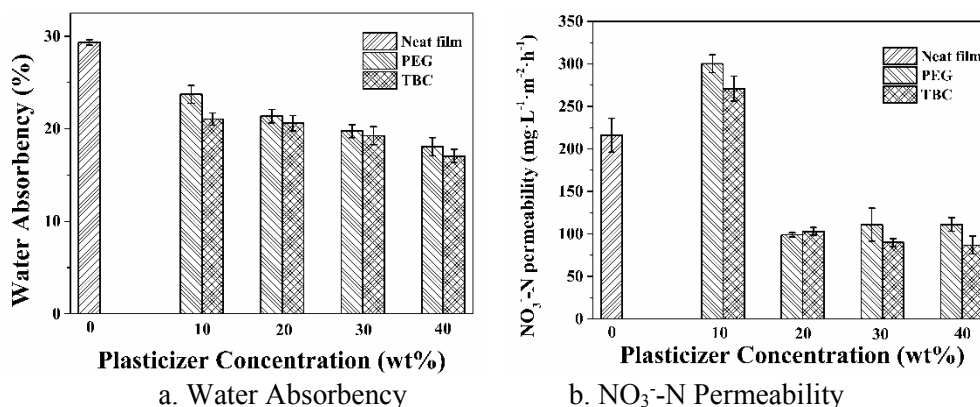


Figure 2. Water absorbency and NO<sub>3</sub>-N Permeability of the PLA film

#### 3.2. Water absorbency and NO<sub>3</sub>-N Permeability

Water absorption test was carried out to study the moisture resistance properties of PLA[13]. Figure 2 shows the water absorbency of those PLA films plasticized by PEG and TBC. It decreased as the increase of plasticizers. Generally, the application of plasticizers led intermolecular and intramolecular linkage of chains between plasticizer and PLA molecules and therefore the hydrophilic groups were reduced. The NO<sub>3</sub>-N permeability also decreased as the increase of plasticizer content, when the concentration was above 10wt %, because of the decreasing affinity between film and water molecular

resulting from the crosslinking reaction between PLA and plasticizer. However, when the plasticizer content is 10wt %, the gap between molecules exist introduced by crosslinking reaction, made the increase of the  $\text{NO}_3^-$ -N permeability rate[14]. The  $\text{NO}_3^-$ -N permeability attained a maximum of  $300.05 \pm 10.47$  and  $270.97 \pm 14.54 \text{ mg} \cdot \text{L}^{-1} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  for the films added PEG and TBC at the concentration of 10%wt, which was good for control release of fertilizer.

#### 4. Conclusion

PLA films were blended with PEG and TBC in various concentration. It was found that the tensile strength had a plasticizer concentration-dependent manner, and the phenomenon was contrary to the elongation at break. The water absorbency decreased as the increase of the plasticizers. The maximal  $\text{NO}_3^-$ -N permeability was observed at the concentration of 10wt%. The value is  $300.05 \pm 10.47$  and  $270.97 \pm 14.54 \text{ mg} \cdot \text{L}^{-1} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  for PEG and TBC respectively. Considered the  $\text{NO}_3^-$ -N permeability, PEG at 10wt% seemed the better plasticizer for PLA used in control release of fertilizer.

#### Acknowledgements

This work was financially supported by Central Public-interest Scientific Institution Basal Research Fund, South China Sea Fisheries Research Institute, CAFS (2016TS07, 2017YB15); The strategic emerging industries and future industrial development of special funds projects in Shenzhen (201608081135), Natural Science Fund of Guangdong (2017A03031 3147).

#### References

- [1] J.P. Deng, J.H. Huang, S.G.Jiang, et al, Condition for bio-floc formation and its effects on *Penaeus Monodon* culture system, Southern Fishies Science. 10 (2014) 29-37.
- [2] X.G. Li, Q. Dou, M.R. Huang, et al, The treatment of wastewater containing mercury ion by copolyaniline sorbent, Southern Fishies Science. 3 (2007) 8-13.
- [3] M.A. Khan, K.W. Kim, M. Wang, et al, Nutrient-impregnated charcoal: an environmentally friendly slow-release fertilizer, Environmentalist. 28 (2008) 231-235.
- [4] J.X. Yu, T.Q. Liu, Preparation and testing of polylactic acid ultra thin fiber membrane as the sustained release material, Advanced Materials Research. 538-541 (2012) 68-71.
- [5] M.S. Shive, J.M. Anderson, Biodegradation and biocompatibility of PLA and PLGA microspheres, Advanced Drug Delivery Reviews. 28 (1997) 5.
- [6] L. Zhang, G. Zhang, J. Lu, et al, Preparation and characterization of carboxymethyl cellulose/polyvinyl alcohol blend film as a potential coating material, Polymer-Plastics Technology and Engineering. 52 (2013) 163-167.
- [7] D.H. Kima, J.S. Park, K.J. Yoon, et al, Studies on the preparation of hydrolyzed starch-g-PAN (HSPAN)/PVA blend films—effect of the reaction with epichlorohydrin, European Polymer Journal. 38 (2002) 1199-1204.
- [8] X.Z. Han, S.S. Chen, X.G. Hu, Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating, Desalination. 240 (2009) 21-26.
- [9] Y. Lemmouchi, M. Murariu, A.M.D. Santos, et al, Plasticization of poly(lactide) with blends of tributyl citrate and low molecular weight poly(d, l-lactide)-b-poly(ethylene glycol) copolymers, European Polymer Journal. 45 (2009) 2839-2848.
- [10] B.W. Chieng, N.A. Ibrahim, M.Z.W.Y. Wan, et al, Poly(lactic acid)/Poly(ethylene glycol) Polymer nanocomposites: effects of graphene nanoplatelets, Advanced Materials Research. 1024 (2014) 93-104.
- [11] K.M. Choi, S.W. Lim, M.C. Choi, et al, Thermal and mechanical properties of poly(lactic acid) modified by poly(ethylene glycol) acrylate through reactive blending, Polymer Bulletin. 71 (2014) 3305-3321.
- [12] V. Tanrattanakul, P. Bunkaew, Effect of different plasticizers on the properties of bio-based thermoplastic elastomer containing poly(lactic acid) and natural rubber, Express Polymer Letters. 8 (2014) 387-396.

- [13] H. Balakrishnan, A. Hassan, M. Imran, et al, Aging of toughened polylactic acid nanocomposites: water absorption, hygrothermal degradation and soil burial analysis, *Journal of Polymers & the Environment*. 19 (2011) 863-875.
- [14] C. Qiang, W.Q. Zhang, L.U. Wei-Jiao, et al, Study on biodegradable chitosan coating materials of fertilizers, *Polymeric Materials Science & Engineering*. (2005).