Preparation and Characterization of Green Composites Based on Sea Lettuce and Poly(lactic acid): Effect of Additives

Toshio YOSHIMURA, and Sae MATSUSHIMA

Faculty of Human Environmental Science, Fukuoka Women's University,
1-1-1 Kasumigaoka, Higashi-ku, Fukuoka 813-8529, Japan

(Received January 06, 2025)

In recent years, major eutrophication has taken place in many seas and coasts in city outskirts all over the world, with the consequent growth of alga commonly known as mucilaginous, composed of compatible species, such as *Ulva armoricana*, *Ulva lactuca*, *Ulva rotundara*, and *Ulva rigida*. Uncontrolled growth of such sea weeds negatively affects coasts worldwide. For example, in the seaside of Hakata Bay in Japan, huge amount of so call sea lettuce such as *Ulva Ohnoi* can be observed every summer and autumn in recent years. Unusual proliferation of such sea lettuce may induce the disruption of ecosystem, insufficient oxygen at bed of the sea, destruction of scenery, and generation of unpleasant smell. Thus, administration of Fukuoka city collects sea lettuce every year by use of special boats and disposes it by landfill at artificial island, "Island City"[1,2]. One of the effective solutions for proliferating sea lettuce is utilization as a feedstock of various functional materials. In our previous studies, development of paper[3], superabsorbent hydrogels[4], surfactant[5] from sea lettuce were investigated. These researches have demonstrated that sea lettuce has the high potentiality as a feedstock of functional materials clearly.

Synthetic polymers produced from petroleum have brought many advantages to the modern society, because they are tough, light, easily processable, and cost effective. However, due to their non-biodegradable property, they are now damaging the ecosystem when disposed to the environment. The development of biodegradable plastics should contribute to the solution of the environmental damage problems. Poly(lactic acid) (PLA) is one of the representative biodegradable thermoplastic polymers with excellent mechanical properties. PLA is produced on a large scale by ring-opening polymerization of lactide, whose original feedstock is naturally occurring polymer such as starch. The biodegradation speed of PLA is quite slow; it degrades in two or three years in the case of landfill. For some applications such as agricultural usage, however, accelerated biodegradation speed of PLA should be preferable. One effective and promising method for the improvement of biodegradability is preparation of green composites based on polymer and natural components.

One potential application for sea lettuce might be natural component for biodegradable plastics such as PLA, because the product composites should equip improved biodegradability. Only a few studies on green composites composed of seaweed and biodegradable plastics such as poly(butylene succinate), however, have been reported so far[6]. On the other hand, green composites based on sea lettuce and PLA has been investigated with some fillers such as glass fiber to enhance mechanical properties, in vain[7].

This paper deals with the green composites from sea lettuce and PLA. Effect of some additives (lysine diisocyanate, lysine triisocyanate, and polyethylene glycol diglycidyl ethers) on mechanical properties of the composites has been investigated. Consequently, in some cases, the product composites exhibited improved mechanical property and good biodegradability, which indicates the promising application on the field of agriculture.

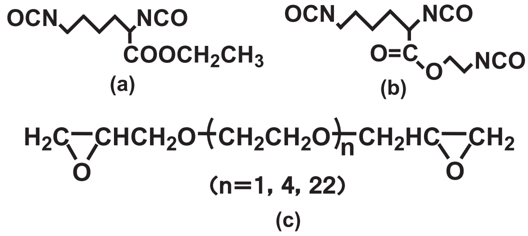

Fig. 1 Chemical Structure of Additives
(a) Lysine diisocyanate (LDI), (b) Lysine triisocyanate (LTI), (c) Polyethylene glycol diglycidyl ether

Experimental

Materials

Naturally proliferating sea lettuce (*Ulva ohnoi*) was collected at Najima in Hakata Bay, repeatedly washed with pure water to remove mud and soils, dried at room temperature, and stored in refrigerator. PLA (MNP-2470) was kindly supplied form NPI Co. Ltd. Cellulose (powder, 20 µm, Aldrich) for standard material of biodegradability test was purchased and used as received. All other chemicals were purchased from commercial sources.

Preparation of composites

The Ulva and PLA were placed in a batch mixer (mechanical blender, Imonex, Kyoto, Japan) at 180°C with blade rotating at a speed of 10 rpm. In the case of the composite whose composition was 5:5 by weight for example, 5 g of PLA and 5 g of Ulva was placed alternately by five times (totally 25 g for PLA and 25g for Ulva) and then, additives were supplied to the mixture. Kneading was conducted for 10 min at the same temperature. After hot mixing, the composites were cooled to room temperature and ground into powder using the kitchen mixer (National MX-X103, Japan).

The kneaded samples were molded into sheets under the pressure of 30 MPa at 180°C with hot press equipment (Imotech, Kyoto, Japan).

Measurement

Hot pressed sheets of the green composites were cut into test specimen whose size was 10 x 50 x 0.6 mm. Each of the samples was dried under vacuum overnight and then stored at room temperature. All tensile and bending tests were performed on testing machine (Minebea LTS-500N-S50, Japan) at a constant crosshead speed of 5.0 mm/min. Five specimens were tested for each composition. Reported results were the average value of higher three results among five.

Biodegradability of the composites was estimated according to the method with the reference to JIS K 6950 in which the sample was placed in the activated sludge at 25°C for 14 days. The activated sludge was kindly supplied from Tataragawa sewage-treatment plant (Fukuoka, Japan), and used as received. The biodegradability was evaluated by monitoring the biological oxygen demand (BOD) using a coulometer (Ohkura Electric Co.Ltd. OM3001, Japan), which detected the consumption of the oxygen during the evaluation. As an alternative evaluation of biodegradability, soil burial test was also carried out by use of the same specimen as evaluation of mechanical properties.

Results and Discussion

Preparation of composites

Two kinds of additives, isocyanate compounds and epoxy compounds ware employed because they are highly reactive to hydroxyl group of polysaccharides in Ulva, which might induce improvement of mechanical properties of green composites based on Ulva and PLA. When lysine diisocyanate and lysine triisocyanate were used as isocyanate additives, the composites solidified and lost its fluidity. In other words, they stuck to the blades of mixing machine. Therefore, further investigation was abandoned. On the other hand, the composites retained their thermoplasticity when epoxy compounds such as ethylene glycol diglycidyl ether (EGDGE) was used as an additive. So, evaluation of mechanical properties was continued by use of composites with epoxy compounds.

Mechanical properties of composites

Fig. 2 shows mechanical properties (tensile strength) of composites based on Ulva and PLA, by changing feed amount of Ulva and PLA (no additives). As is obvious from Fig. 2, tensile strength gradually decreased with the feed amount of Ulva. But their decrease was rather slow until 5:5 of Ulva and PLA. Therefore, further investigation was carried out keeping the feed ratio of 5:5.

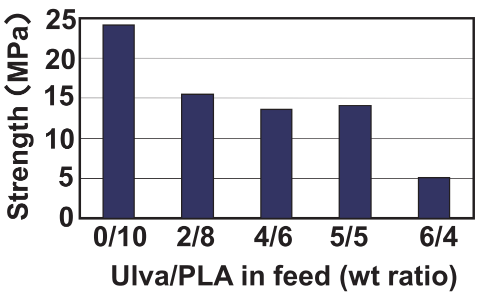

Fig. 2 Tensile Strength of Composites based on Ulva/PLA

Next, effect of chemical structure of epoxy compounds on mechanical properties was investigated (Fig. 3). The feed amount of epoxy additives was constantly 1.0% to the composites. As is obvious from Fig. 3, the mechanical strength of the composites was improved in both tensile and flexural tests compared to the case without the additive, when the epoxy compound was used as an additive. Among them, EGDGE (n=1) was the most effective to obtain the highest value, which indicates that shorter chemical structure of diepoxy compound is more preferable for the improvement of mechanical strength.

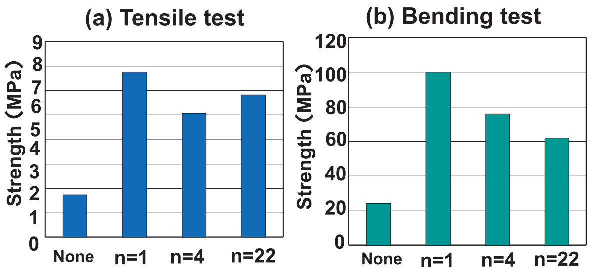

Fig. 3 Effect of Epoxy Compounds on Mechanical Strength of Ulva/PLA-based Composites

Effect of EGDGE on mechanical properties of the composites was examined by changing its feed amount (Fig. 4). Consequently, 0.5% was the most effective for the improvement of mechanical strength of the composites, for both of tensile and bending.

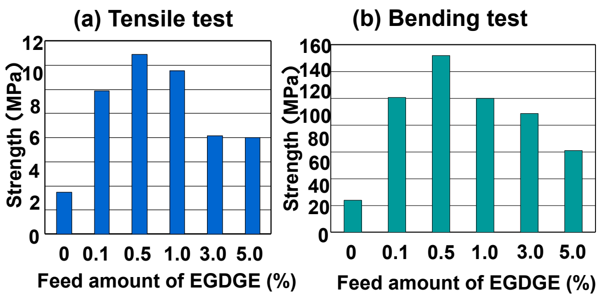

Fig. 4 Effect of Feed Amount of EGDGE on Mechanical Strength of Ulva/PLA-based Composites

Then, we examined the evaluation of biodegradability of the composite when epoxy compounds were used as additives. As shown in Fig.5, the higher the amount of additive, the better the biodegradability, as evaluated by measuring biochemical oxygen demand (BOD) in activated sludge. Initially, there was concern that modification with epoxy compounds would reduce the biodegradability of the composites, but quite interesting results were obtained; biodegradability was promoted with the addition of the epoxy compounds.

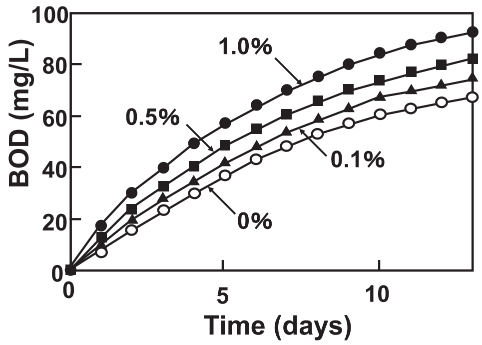

Fig. 5 Biodegradability of Ulva/PLA-based Composites based on BOD in Activated Sludges

In the soil burial test, the composite sample without the additive collapsed after 3 weeks of burial; after 4 weeks, the one with 3% and 5% of the additive collapsed (Fig. 6). The remaining 0.1%, 0.5%, and 1% continued to be buried; after 6 weeks, those with 0.1% and 1% of the additive collapsed. The remaining 0.5% continued to be buried; after 8 weeks, the sample wit 0.5% had collapsed and all specimens had collapsed (Fig.6). In sharp contrast to the biodegradability

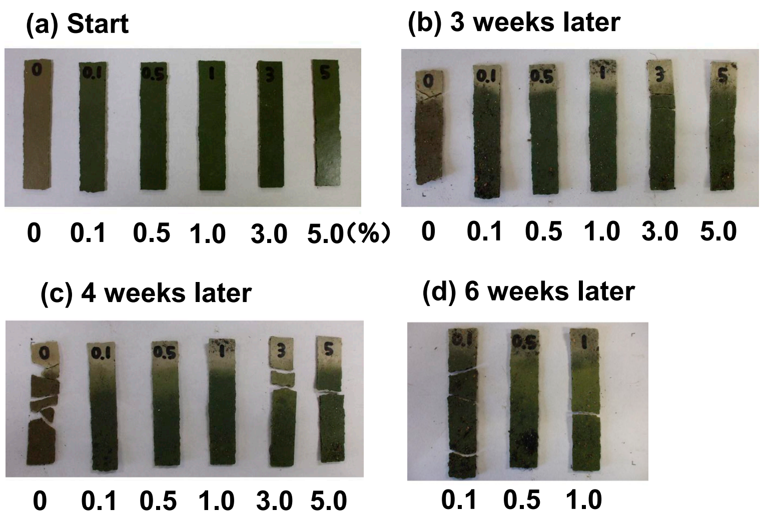

Fig. 6 Biodegradability of Ulva/PLA-based Composites based on Soil Burial Test

test result in activated sludge, the better the mechanical property evaluation, the longer the shape retention period.

Summary

In the Ulva/PLA-based green composites, effect of additives was investigated to improve mechanical properties by use of some isocyanate and epoxy compounds. Mechanical strength was improved by adding epoxy compounds. As a result of examining the type and amount of epoxy compound, 0.5% of the compound with n = 1 (EGDGE) was most effective, and it had good biodegradability in both the BOD and soil burial tests. These results indicate that the composites in the present study have potentiality in many applications such as agricultural use.

References

1) T. Yoshimura, K. Wakamatsu, *Kankyo (Kyushu daigaku tokusyuhaieki syorisisetsu koho)*, **21**, 3 (2006).
2) T. Yoshimura, D. Tatsumi, R. Fujioka, *News Letter of Consortium Fukuoka*, **4**, 11 (2011).
3) T. Yoshimura, *Report on utilization of sea lettuce proliferating at Hakata Bay*, *City of Fukuoka*, 35 (2005).
4) T. Yoshimura, N. Hirao, R. Fujioka, *Polymers from Naturel Resources*, **7**, 33 (2016).
5) R. Fujioka, T. Higashiyama, N. Takami, Y. Furuta, T. Yoshimura, *J. Home Economics of Japan*, **61**, 725 (2010).
6) T. Yoshimura, M. Iwami, and R. Fujioka, *Bulletin of Faculty of Human Environmental Science, Fukuoka Women's University*, **44**, 23-27 (2013).
7) T. Yoshimura, K. Miyajima, and R. Fujioka, *Bulletin of Faculty of Human Environmental Science, Fukuoka Women's University*, **45**, 35-38 (2014).