Preparation and Characterization of Green Composites Based on Shells and Poly(lactic acid)

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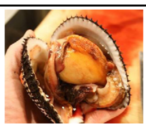
Fukuoka, with its northern coast facing the Genkai Sea, is one of Japan's richest areas in terms of marine resources. In addition to fish, shellfish cultivation and fishing are also thriving. Oysters from Itoshima and other areas in the prefecture are well-known, and in recent years, cultivation of Akoya pearl oysters has begun by Mikimoto, a long-established pearl cultivation company in Japan, in Ainoshima[1-3]. There are a variety of shellfish species that can be caught in the waters around Fukuoka, as shown in Table 1. Thus, the shellfish industry is thriving in the waters around Fukuoka, but most of the shells generated in this process are discarded so far. In response to this situation, the Fukuoka Industrial Technology Center, in cooperation with some local companies, is studying the effective use of shells[4]. Currently, studies are underway to commercialize the use of crushed shells as a soil conditioner, because the main component of shells is calcium carbonate.

Table 1 Current status of shellfish in the sea around Fukuoka

Oyster		**The Itoshima area is famous for its oyster farming.**
Akoya pearl oyster		**Ainoshima is excellent for pearl cultivation. Mikimoto, a major jewelry manufacturer, began pearl cultivation in 2007.**
Red clam		**Red clams are caught in the Ariake Sea. The shells are collected and processed into organic lime.**

As mentioned above, there are few examples of effective use of shells, and no studies have been conducted on shells other than crushing them and using them as soil conditioners. On the other hand, composites of organic materials such as green seaweed, *Ulva* and biodegradable plastic such as polybutylene succinate (PBS) have been studied in our previous studies[5,6].

In the present study, preparation of novel composites of shell powder and poly(actic acid) (PLA), and their properties have been examined, to clarify the effectiveness of wasted shells as a recycling material. In addition, unlike previous studies, investigation of composites comprising PLA and inorganic substances should be a quite interesting project, because organic substances were mainly used for the components of the PLA-based composites.

Experimental

Materials

Four kinds of shell powder (baked oyster, small oyster, Akoya pearl oyster, and red shell) were kindly provided by The Industrial Technology Center of Fukuoka Prefecture. 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 shell powder 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 3:7 by weight for example, 7 g of PLA and 3 g of shell powder was placed alternately by five times (totally 35 g for PLA and 15g for shell powder) and then, 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

The microstructure of a composite was observed using a scanning electron microscope (SEM) with Keyence VE-9800 at the required magnification and with accelerating voltage of 20 kV. A specimen from tensile test was mounted on an aluminum stub, and the fractured surface was observed at the magnitude of 100 and 500.

Hot pressed sheets of the green composites were cut into test specimen whose size was 10 x 50 x 0.6 mm^3. Each of the samples was dried under vacuum overnight and then stored at room temperature. All tensile 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.

Particle size distribution of shell powder was measured with Shimadzu Laser Diffraction Particle Size Analyzer SAND-300V.

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.

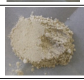
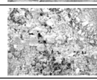
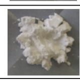
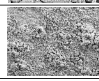
Thermogravimetric analysis was conducted in nitrogen atmosphere with HITACHI STA7200; heating rate was 10°C /min, and temperature range was from room temperature to 500°C.

Results and Discussion

Preparation of composites

First, the shape and size of the grains of crushed shells were checked. The appearance, scanning electron microscope (SEM) images, and average particle size of the crushed shells were listed in Table 2. From the SEM photographs, the shape and size of the crushed shell particles are different from each other. And the same sample does not have uniform grain shape and size. The calcium carbonate, on the other hand, is almost uniform in grain shape and size. Comparing the average grain size of crushed shells and calcium carbonate, the average grain size of baked oysters and small oysters, which have larger grain size, is about twice as large as that of red shells, Akoya pearl oysters, and calcium carbonate, which have smaller grain size. From the above, it can be seen that the grain shape and grain size of crushed shells differ from each other.

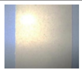
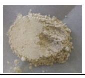
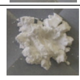
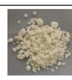
Table 2 The shape and size of the grains of crushed shells

Sample	Appearance	SEM photograph	Diameter (μm)
Baked oyster			57.1
Small oysters			67.9
Red clam			24.0
Akoya pearl oyster			35.4
Calcium carbonate			31.4

Next, Table 3 shows the appearance of crushed shells, composites, and flat plates, respectively. The color of the crushed shells is all milky white, but the intensity of the color varies slightly among the different types. As shown in the table, the intensity of coloration of the composite powder and slabs corresponds to the color of the crushed shells. In other words, the intensity of the coloring of the slabs varies depending on the color of the crushed shells.

The tensile test results for composites with PLA alone,

Table 3 Appearance of composites

Sample	powder	composite	plate
Baked oyster			
Small oysters			
Red clam			
Akoya pearl oyster			
Calcium carbonate			

baked oysters, small oysters, Akoya pearl oysters, red shells, and calcium carbonate are shown in Fig.1. This shows the composite's stress at break. The average of the top three stress at break for polylactic acid alone was 50 MPa, whereas the average breaking point stresses for shell-based composites and calcium carbonate composites were around 30 MPa. There was little difference in strength between the different types of shells. And there was no correlation between the strength of the composite and the average grain size or the intensity of the coloring of the flat plate. Therefore, it can be said that the strength of the composite was hardly affected by the type of shells, the grain size of the crushed shells, or the density of the coloring of the flat plate.

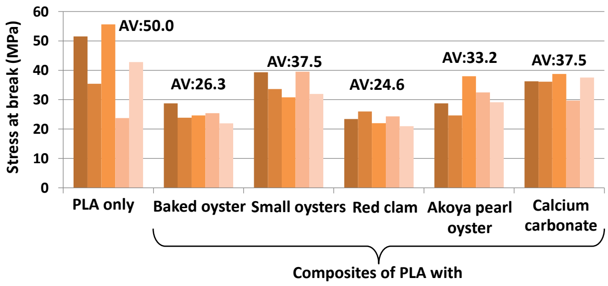


Fig. 1 Tensile test results (stress at break)

Fig. 2 exhibits the elastic modulus values for PLA alone and for each composite. The elastic modulus values of the shell composite and calcium carbonate composite are higher than that of PLA. This indicates that compositing with shells has the effect of improving the elastic modulus.

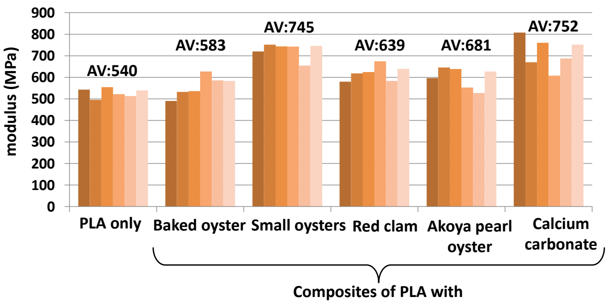


Fig. 2 Tensile test results (modulus of elasticity)

The biodegradability evaluation of shell composites and cellulose was conducted. As shown in Fig. 3, cellulose showed good biodegradability, but none of the shell composites biodegraded at all. As PLA alone also exhibited no biodegradability, so these experimental results indicate that the addition of shell crushed did not enhance the biodegradation speed of composites.

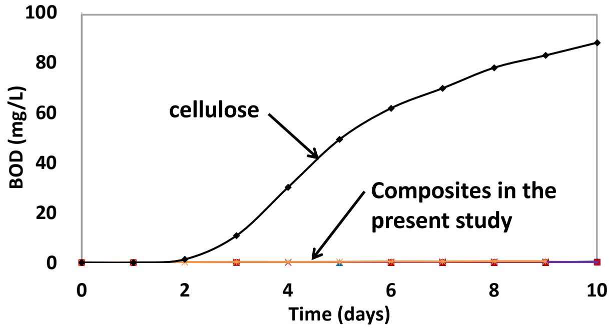


Fig. 3 Biodegradability of composites

The thermogravimetric analysis results of crushed shells and shell-based composites are shown in Fig. 4. The left graph shows the results for crushed shells and the right graph shows the results for shell-based composites. The weight loss due to heat was negligible for the crushed seashell composite, and the results for the composite corresponded to that of the crushed seashell composite. It is clear from the graph that while there is some difference in the thermal stability of the shell-crushed composites, there is little difference in the thermal stability of the composites.

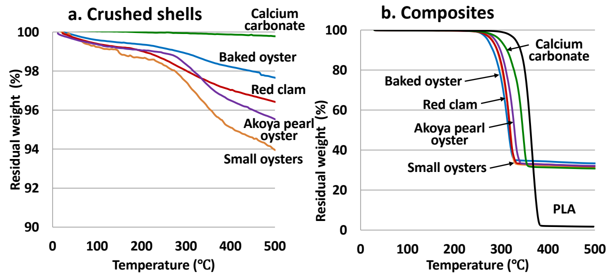


Fig. 4 Thermogravimetric analysis of crushed shells and composites

Summary

With the goal of making effective use of shell crushed material, we investigated the development of shell-based green composites using baked oysters, red shells, Akoya oysters, and polylactic acid, and obtained the following findings.

The color of the shell-based composites corresponded to the color of the shell crushed material. The strength of the composites was largely unaffected by the type of shell, the grain size of the shell crushed material, or the intensity of the coloring of the composite. On the other hand, the elastic modulus of the composite increased with the addition of shells. In addition, the addition of shell crushed material had no accelerating effect on the biodegradation rate of the composite.

References

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