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Hydrolysis control by introduction of photodissociable protecting groups in PLA as matrix of green composite materials

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This study proposed an environmental-friendly method to control the hydrolytic behavior of poly-lactic acid (PLA) as matrix of green composite materials by the suppression of biodegradability during usage and the acceleration of biodegradability after disposal. Here, the suppression and acceleration of biodegradability was tried by introducing photodissociable protecting groups into carboxyl end groups and deprotecting using the ultraviolet ray irradiation, respectively. We selected o-nitrobenzyl alcohol as the photodissociable protecting group. We conducted the Fourier transform infrared measurement and tensile tests in order to verify the effect of the hydrolysis control proposed in this study. As results, photodissociable protecting groups could be successfully introduced into carboxyl end groups of PLA. It is considered that the suppression of biodegradation during usage in PLA could be achieved by the introduction of photodissociable protecting groups tried in this study. The deprotection of photodissociable protecting groups was successfully and efficiently induced by the ultraviolet ray irradiation employed in this study, resulting in the acceleration of hydrolysis. In order to maximize the hydrolysis control function, it is desired that the combination and reaction environment of biodegradable polymers and photodissociable protecting groups could be optimized using the inverse problem analysis based on the molecular dynamics and the experimental results, in future.

Keywords: green composites; PLA matrix; hydrolysis control; photodissociable protecting groups

1. Introduction

In recent years, the application of advanced composite materials has been widely and rapidly expanding to advanced technologies, such as primary structures of aircrafts and automobiles. However, considering global environmental problems, it is necessary to develop sustainable materials, which would not induce the environmental pollution by their disposal. Here, petroleum-derived commodity polymers, which are generally used as matrix of advanced composite materials, are usually incinerated, buried or recycled after their disposal. In the case of incineration, its high combustion calorie often damages incineration furnaces. In addition, harmful gases are sometimes produced. In the case of landfill disposal, the large landfill site is needed owing to the high specific

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*Corresponding author. Email: mototsugu@neptune.kanazawa-it.ac.jp volume of undegradable polymers. In addition, there is the possibility of the spill of hazardous materials. In the case of recycling, the material recycling of products and the chemical recycling by conversion to other chemical substance induces the oversupply and shortage of raw materials, respectively.

The development of environmental-friendly composite materials, so-called green composites, is one of the powerful approaches to solve those global environmental problems. Green composites are mainly composed of biodegradable polymers and high-strength natural fibers. Biodegradable polymers are ideally degraded to water and carbon dioxide by hydrolysis and enzymolysis. A number of studies have been conducted aiming to give superior performance, high functionality and high added value to green composites.[1–17] Almost all of them aim to improve the mechanical properties of green composites by improvement of fabrication process,[1–7] modification of biodegradable polymers,[8–11] surface-treatment of natural fibers,[12–17] and so on. However, the prevention of hydrolytic degradation by air moisture before the product life cycle and the rapid degradation after disposal should be essentially consistent in biodegradable green composites. In other words, it is desired that the hydrolysis control function, consisting of the suppression of biodegradation during usage and the acceleration of biodegradation after disposal, is created for green composites using environmental-friendly methods.

Generally, the suppression of biodegradation can be achieved by the improvement of crystallinity in biodegradable polymers.[18] On the other hand, the higher crystallinity decreases the mobility of molecular chains and the diffusibility of water molecules.[18] Therefore, it would be difficult to achieve the acceleration of biodegradation after disposal in green composites by the approach to improve the crystallinity of biodegradable polymers as matrix. The hydrolysis in poly-lactic acid (PLA), one of the typical biodegradable polymers, originates from carboxyl end groups, existing in amorphous region and acting as autocatalysis.[18,19] Here, it can be hypothesized that the hydrolysis control function could be created in PLA by introducing deprotective molecular caps into carboxyl end groups and consequently controlling their autocatalytic activity. From this view point, Chandy and Sharma [20] suppressed the biodegradation of PLA by introducing carbodiimide, one of diisocyanate-condensed plastics, into carboxyl end groups, even though carbodiimide caps are not deprotective. Kusunoki and Fukami [21] introduced alkynyl methyl groups, which can be deprotected using strong acids such as trifluoroacetic acid in the presence of metal complex of $CO_2(CO)_8$ or metals, into carboxyl end groups of PLA. These are novel trials challenging to consist the suppression of biodegradation during usage and the acceleration of biodegradation after disposal in biodegradable polymers. As a next step, it is desired that the hydrolysis control function is achieved by the environmental-friendly method.

Here, we focused on photodissociable protecting groups as deprotective molecular caps of carboxyl end groups of PLA. Photodissociable protecting groups can be deprotected by the irradiation of ultraviolet rays. Yamaguchi et al. [22] introduced 2-nitrobenzyl groups into alkyl side chains of phospholipids, and then achieved the selective releasing process of inclusions by the irradiation of ultraviolet rays. In this study, photodissociable protecting groups were introduced into carboxyl end groups of PLA, and then the possibility to create the hydrolysis control function was studied by the suppression of autocatalytic activity and the deprotection by the irradiation of ultraviolet rays.

2. Experimental methods

2.1. *Introduction of photodissociable protecting groups into PLA*

PLA used in this study was Ecodear (Toray Industries, Inc.). Photodissociable protecting group used in this study was o-nitrobenzyl alcohol (Wako Pure Chemical Industries, Ltd.). Chemical structures of PLA and o-nitrobenzyl alcohol are shown in Figure 1. In order to disperse photodissociable protecting groups in PLA uniformly, it is necessary to decrease the viscosity of PLA. In this study, dichloromethane was used for the dissolution of PLA. Even though the dissolution of PLA into dichloromethane was not necessary for the preparation of neat PLA, the dissolution process into dichloromethane was employed for neat PLA, in order to compare the experimental results under the same condition.

First, fragments of PLA sheet with the size of $1 \times 10^{-4}\,\mathrm{m}^2$ were gradually put into dichloromethane while stirring at the rotation speed of 250 rpm for 600 s. Here, the weight ratio of PLA to dichloromethane was 1–10. After stirring, o-nitrobenzyl alcohol was put into the solution, followed by stirring for 300 s. Here, the weight fraction of o-nitrobenzyl alcohol to PLA was about 2 wt.%. Then, this solution was poured into ethanol, in order to precipitate PLA. Precipitated PLA was dried at 0.03 MPa in a vacuum equipment for 24 h, followed by drying at 313 K in a thermostatic oven for 5 h. Here, PLA without and with the introduction of photodissociable protecting groups is named as neat PLA and modified PLA, respectively. In order to confirm if photodissociable protecting groups were introduced into PLA or not, spectral analyses of neat

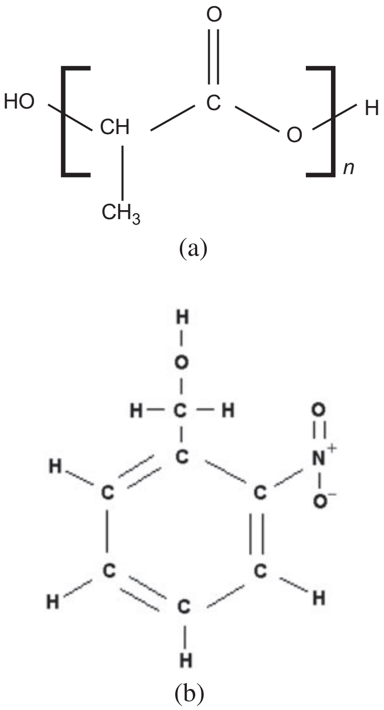


Figure 1. Chemical structures of PLA and o-nitrobenzyl alcohol. (a) PLA. (b) o-nitrobenzyl alcohol.

PLA and modified PLA were conducted using a Fourier transform infrared (FTIR) spectrophotometer (Horiba, Ltd., FT-720).

2.2. Preparation of PLA sheets

In this study, both neat and modified PLA sheets were prepared using a hot-pressing device with a foot pump (Techno-supply, Inc., G-12). First, small fragments of PLA were placed on a kapton sheet (110 mm × 110 mm, thickness of 0.05 mm) on a mold-release-agent-coated die made of stainless steel, followed by the arrangement of a mold-release-agent-coated spacer, another kapton sheet and another stainless steel die, as shown in Figure 2. Then, hot-pressing was conducted under the condition of 0–0.6 MPa at 473 K for 600 s, followed by hot-pressing under the condition of 7.2 MPa at 473 K for 300 s. Generally, the hydrolysis of PLA originates from amorphous regions.[18,19] This means that higher amorphous ratio induces higher hydrolysis rate in PLA. In this study, higher amorphous ratio inducing higher hydrolysis rate is preferable, because the effect of hydrolysis control would become evident. Thus, finally, rapid cooling was conducted using refrigerants. The crystallinity of molded PLA sheets was measured using a differential scanning calorimetry (DSC) (Rigaku Corporation, DSC8230). Here, alumina powders were used as the standard reference material, and heating rate was 1.67 K/s.

2.3. Hydrolysis and deprotection

Test pieces with the width of 5 mm and length of 50 mm were cut from molded PLA sheets. The hydrolysis of these test pieces was conducted by immersing into distilled water at 343 K. It is known that the hydrolysis rate of PLA dramatically increases at more than about 330 K.[23] In order to conduct the acceleration test, the temperature of distilled water was selected as 343 K. After certain periods, test pieces were removed from distilled water, and dried at 315 K for 5 h using a thermostatic oven. Even though 72 h immersion sometimes caused the breakage of test pieces into small pieces, test pieces after 48 h immersion retained their almost original shapes without breakage.

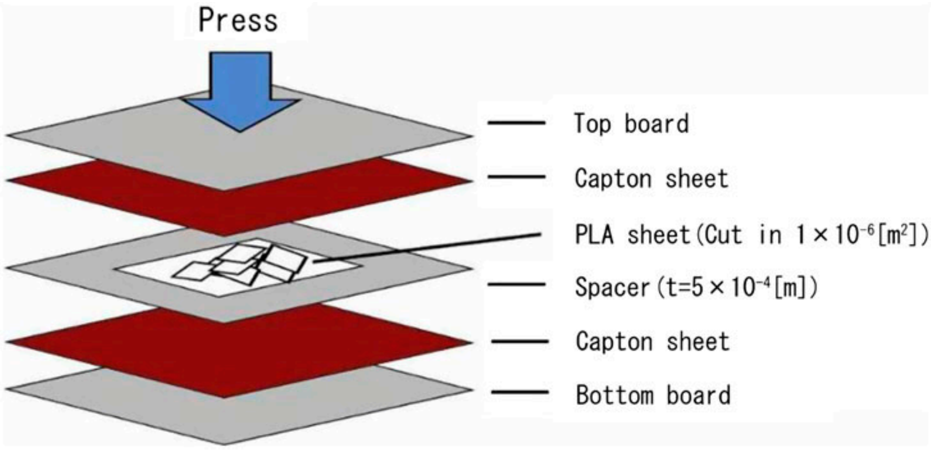


Figure 2. Schematic drawing of hot-pressing setup.

Thus, we decided the maximum immersion period in this study as 48 h. The deprotection of photodissociable protecting groups was conducted by the irradiation of an ultraviolet ray of the wavelength of 365×10^{-9} m for 1800 s.

2.4. Tensile test

In order to evaluate the effect of the introduction of photodissociable protecting groups on the strength of PLA, tensile tests were conducted using a servo-hydraulic testing machine (Shimadzu Corporation, EHF-EB5KN-10LAL) installing a load cell with the capacity of 5 kN, in conformity to JIS K7113. The crosshead speed was 1.67×10^{-5} m/s. Here, tabs (thickness: 1 mm) made of glass-fiber-reinforced plastics were pasted on the both ends of test pieces, as shown in Figure 3.

3. Results and discussion

3.1. Verification of introduction of photodissociable protecting groups and crystallinity of PLA

Infrared absorption spectra of neat PLA and modified PLA were analyzed using a FTIR, as shown in Figure 4. If o-nitrobenzyl alcohol could be introduced into carboxyl end groups ideally, the spectral strength characteristic in o-nitrobenzyl alcohol would be increased, whereas that corresponding to carboxyl groups decreased. As a result, the spectral strengths corresponding to nitro groups (about 1500 cm^{-1}) and hydroxyl groups (about 3500 cm^{-1}) were increased by introducing o-nitrobenzyl alcohol. This means that o-nitrobenzyl alcohol could be introduced into PLA. On the other hand, the spectral strength corresponding to carboxyl groups (1700–1900 cm^{-1}) was decreased by introducing o-nitrobenzyl alcohol. This means that o-nitrobenzyl alcohol could be successfully introduced into carboxyl end groups of PLA.

However, the spectral strength corresponding to ester bonds (1000–1500 cm^{-1}) was decreased by introducing o-nitrobenzyl alcohol. This suggests that photodissociable protecting groups penetrated into PLA molecular chains during polymerization of PLA, resulting in the disturbance of ester bonds. In addition, the spectral strength corresponding to methyl groups (about 3000 cm^{-1}) was also decreased by introducing o-nitrobenzyl alcohol. This means that photodissociable protecting groups were also introduced into methyl side groups of PLA molecular chains, suggesting that selective introduction of protecting groups only into carboxyl end groups could not be achieved.

In order to verify if the crystallinity of molded PLA sheets is low or not, the crystallinity measurement was conducted using a DSC. Here, PLA was heated with alumina

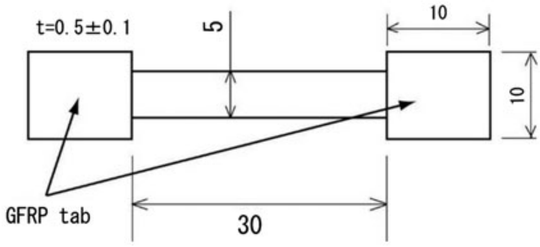


Figure 3. Schematic drawing of tensile specimen (dimensions are in mm).

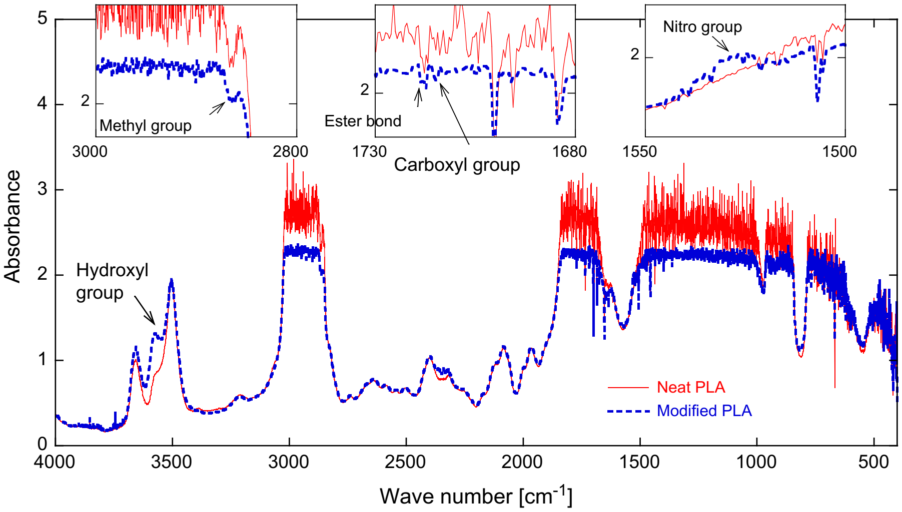


Figure 4. Infrared absorption spectra of neat and modified PLAs without immersion.

powders as the standard reference material. From the difference of thermal capacity between PLA and alumina powders, crystallization enthalpy, ΔHc, and melting enthalpy, ΔHm, can be evaluated. Here, areas of exothermic and endothermic peaks in DSC curves (Figure 5) correspond to ΔHc and ΔHm, respectively. The crystallinity, Xc, can be evaluated using the following equation.

$$Xc = 100 \times (\Delta Hm - \Delta Hc)/93 \tag{1}$$

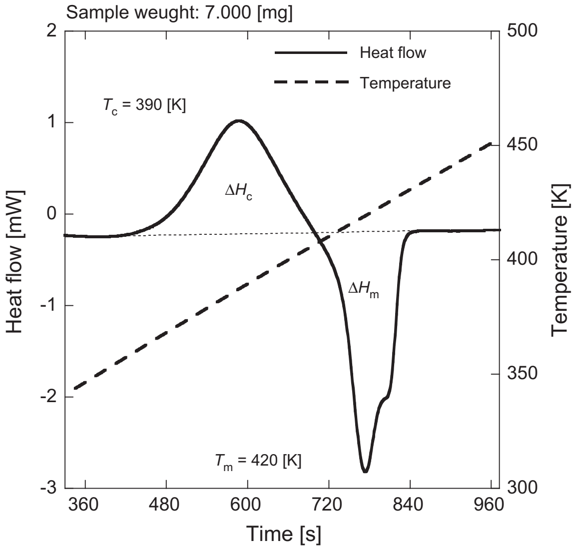


Figure 5. Typical heat flow curve of molded PLA sheet.

Here, the denominator of this equation, ‘93’, is the melting enthalpy of PLA with the crystallinity of 100%.[24] Figure 6 shows the crystallinity of PLA sheets rapidly cooled using refrigerants and slowly cooled at about 0.025 K/s as a reference. The crystallinity of rapidly cooled PLA sheets was about 0.75 %, suggesting that the amorphous ratio of molded PLA was enough high.

3.2. *Effect of introduction of photodissociable protecting groups on tensile strength*

Figure 7 shows typical stress–strain curves for neat PLA and modified PLA without immersion. Figure 8 shows the elastic modulus and tensile strength of neat PLA and modified PLA without immersion. The average value of elastic modulus of neat PLA and modified PLA without immersion was about 2.2 GPa and about 1.7 GPa, respectively. Even though the reason why the introduction of photodissociable protecting groups decreased the elastic modulus of PLA cannot be understood, it is guessed that the disturbance of ester bonds might change the length of PLA molecular chains. The simulation for polymerization of PLA and chemical reaction between PLA and o-nitrobenzyl alcohol, based on the molecular dynamics, is desired as the next step. On the other hand, the average value of tensile strength of neat PLA and modified PLA without immersion into distilled water was about 38 MPa and about 42 MPa, respectively. Thus, the introduction of photodissociable protecting groups, employed in this study, did not affect the tensile strength of PLA. Therefore, the tensile strength is used for the discussion on the effect of the introduction of photodissociable protecting groups on the mechanical properties of PLA, in this study.

Figure 9 shows typical stress–strain curves for neat PLA and modified PLA after immersion. Figure 10 shows the influence of immersion on the tensile strength of neat and modified PLAs. For both specimens, the tensile strength tends to decrease with increasing immersion time, suggesting the gradual progress in hydrolysis. After 48 h immersion, the decreasing ratio in tensile strength was about 54% for modified PLA

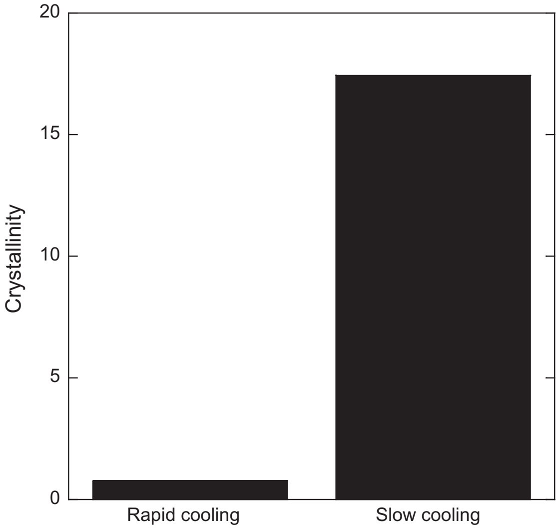


Figure 6. Crystallinity of PLA sheet.

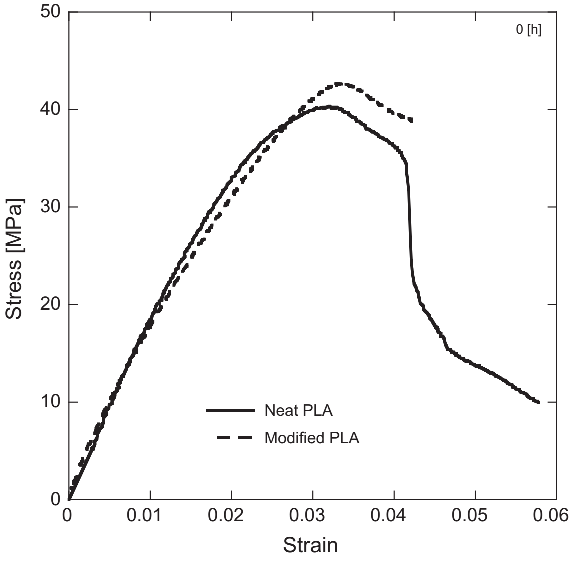
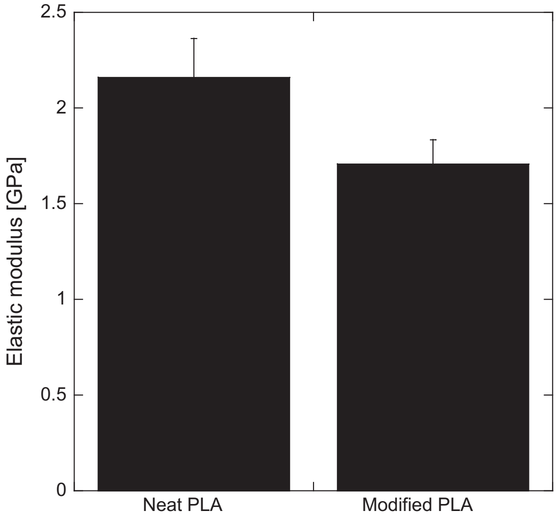


Figure 7. Typical stress–strain curves for neat PLA and modified PLA without immersion.

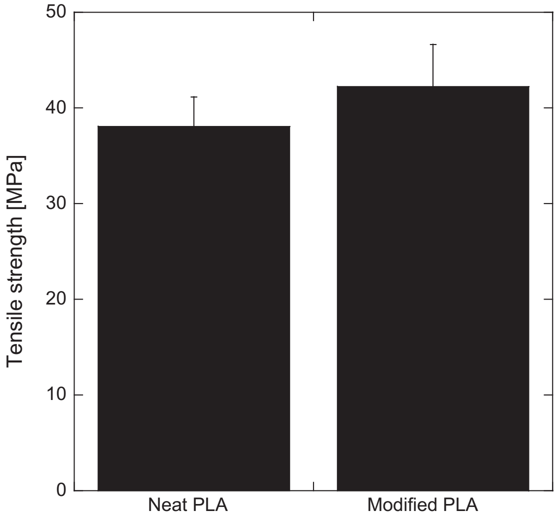
whereas 90% for neat PLA. Thus, the hydrolytic decrease in tensile strength was greatly suppressed by the introduction of photodissociable protecting groups. Therefore, it is considered that the suppression of biodegradation during usage in PLA could be achieved by the introduction of photodissociable protecting groups tried in this study. However, the tensile strength of modified PLA also decreased by hydrolysis. This means that unprotected carboxyl end groups still existed after the introduction of photodissociable protecting groups. In order to maximize the hydrolysis control function, it is desired that the combination and reaction environment of biodegradable polymers and photodissociable protecting groups could be optimized using the inverse problem analysis based on the molecular dynamics and the experimental results.

3.3. *Effect of deprotection of photodissociable protecting groups on tensile strength*

Figure 11 shows the effect of the irradiation of ultraviolet ray on the tensile strength of neat PLA and modified PLA. Here, the irradiation of ultraviolet ray was conducted after 24 h immersion. For neat PLA, the tensile strength after irradiation was 1.3 times of that before irradiation. For modified PLA, the tensile strength after irradiation was 1.0 times of that before irradiation. Since the variation in tensile strength after 24 h immersion was the largest as shown in Figure 10, these values would be within the range of scattering, suggesting that the irradiation of ultraviolet ray employed in this study was not strong enough to give damage to PLA molecular chains. Figure 12 shows specimen morphologies of neat and modified PLAs before immersion, after immersion, and after irradiation. The foxing of modified PLA was uniform and much evident than that of neat PLA. It is suggested that this evident foxing in modified PLA was owing to the deprotection of introduced photodissociable protecting groups. Therefore, it is considered that the photodissociable protecting groups were uniformly introduced into PLA.



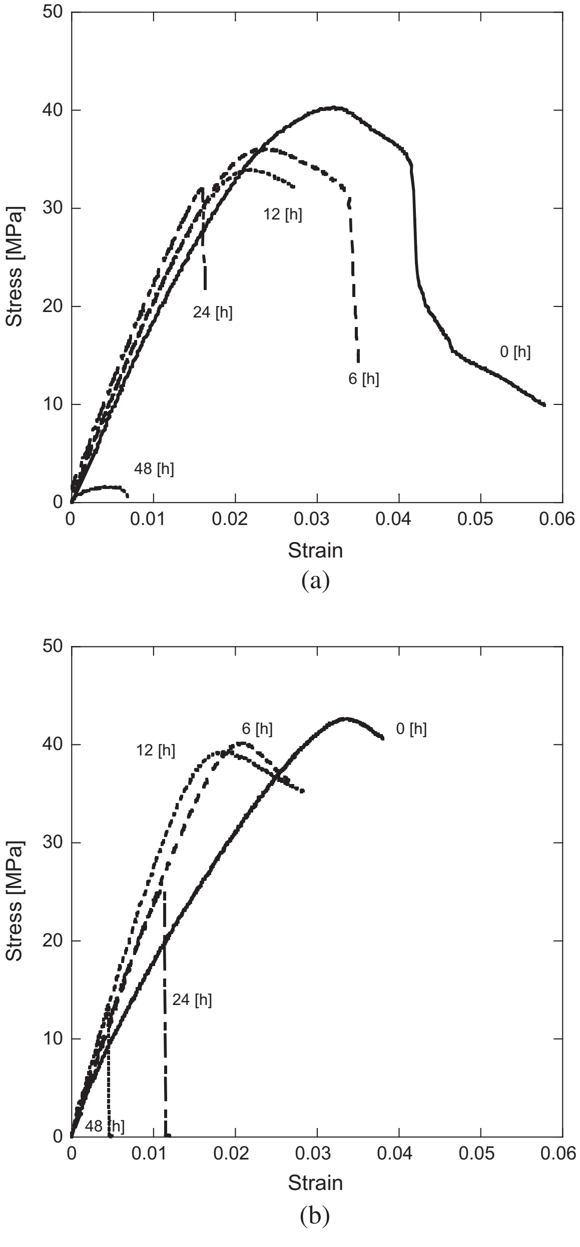
(a)



(b)

Figure 8. Elastic modulus and tensile strength of neat and modified PLAs without immersion. (a) Elastic modulus. (b) Tensile strength.

In order to investigate the influence of deprotection of photodissociable protecting groups used in this study, modified PLA specimen was irradiated by ultraviolet ray after 24 h immersion, and then was immersed for more 24 h, followed by drying and tensile test. Tensile strength of this specimen was lower than that of modified PLA after 48 h immersion (see Figure 10). As described above, the ultraviolet ray irradiation employed in this study was not strong enough to give damage to PLA molecular chains. Therefore, this result suggests that photodissociable protecting groups could be removed by the ultraviolet ray irradiation and consequently the autocatalytic function



(a)

(b)

Figure 9. Typical stress–strain curves for neat and modified PLAs after immersion. (a) Neat PLA. (b) Modified PLA.

of carboxyl end groups could be activated. This means that the deprotection of photodissociable protecting groups was successfully induced by the ultraviolet ray irradiation employed in this study, resulting in the acceleration of hydrolysis. In addition, the decrease in the tensile strength of modified PLA after 24 h immersion was about 29 MPa by the irradiation and following 24 h immersion. Since the decrease in the tensile

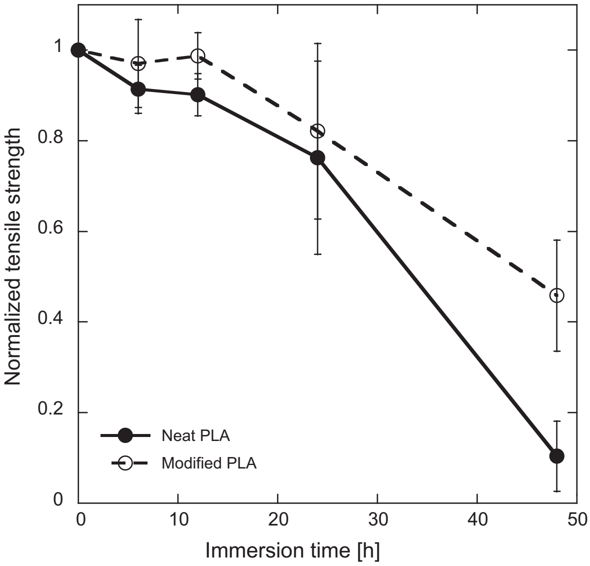


Figure 10. Influence of immersion on tensile strength of neat and modified PLAs.

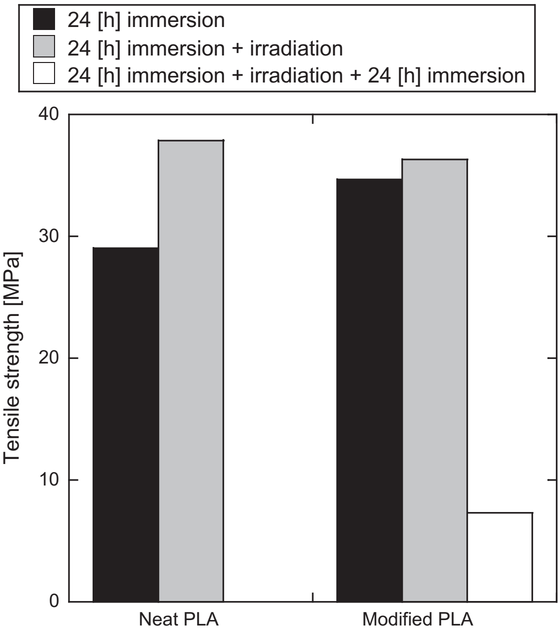


Figure 11. Effect of irradiation of ultraviolet ray on tensile strength of neat and modified PLAs.

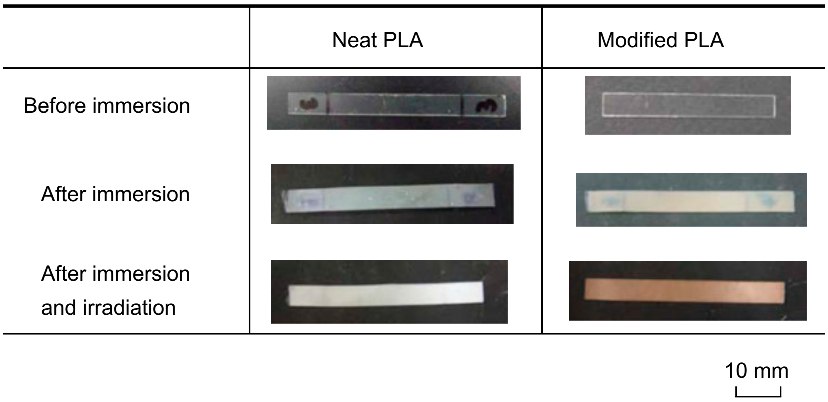


Figure 12. Specimen morphologies of neat and modified PLAs.

strength of neat PLA after 24 h immersion was about 25 MPa by more 24 h immersion, it can be considered that the deprotection of photodissociable protecting groups was efficiently conducted by the method employed in this study.

Therefore, it is considered that the acceleration of biodegradation after disposal in PLA could be achieved by the deprotection of photodissociable protecting groups tried in this study. In future, it is desired that the introduction efficiency of photodissociable protecting groups could be optimized by the molecular reaction design between biodegradable polymers and photodissociable protecting groups based on the molecular dynamics, and then the practicability of the hydrolysis control proposed in this study would be guaranteed.

4. Conclusions

This study proposed an environmental-friendly method to control the hydrolytic behavior of PLA as matrix of green composite materials by the suppression of biodegradability during usage and the acceleration of biodegradability after disposal. Here, the suppression and acceleration of biodegradability was tried by introducing photodissociable protecting groups into carboxyl end groups and deprotecting using the ultraviolet ray irradiation, respectively. We selected o-nitrobenzyl alcohol as the photodissociable protecting group. We conducted the FTIR measurement and tensile tests in order to verify the effect of the hydrolysis control proposed in this study. The conclusions are summarized below:

(1) Photodissociable protecting groups could be successfully introduced into carboxyl end groups of PLA. However, it was suggested that photodissociable protecting groups penetrated into PLA molecular chains during polymerization of PLA, resulting in the disturbance of ester bonds. In addition, photodissociable protecting groups were also introduced into methyl side groups of PLA molecular chains.

(2) The introduction of photodissociable protecting groups and the irradiation of the ultraviolet ray, employed in this study, did not affect the tensile strength of PLA.

(3) It is considered that the suppression of biodegradation during usage in PLA could be achieved by the introduction of photodissociable protecting groups tried in this study. However, unprotected carboxyl end groups still existed after the introduction of photodissociable protecting groups.
(4) The deprotection of photodissociable protecting groups was successfully and efficiently induced by the ultraviolet ray irradiation employed in this study, resulting in the acceleration of hydrolysis.

These conclusions suggest that the hydrolysis control proposed in this study would be possible. On the other hand, the selective introduction of protecting groups only into carboxyl end groups could not be achieved. In addition, unprotected carboxyl end groups still existed after the introduction of photodissociable protecting groups. It is desired that the introduction efficiency of photodissociable protecting groups could be optimized by the molecular reaction design between biodegradable polymers and photodissociable protecting groups based on the molecular dynamics and the experimental results, in order to guarantee the practicability of the hydrolysis control proposed in this study.

Acknowledgment

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