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Photo-activated chlorine dioxide oxidized polylactic acid – washi paper composites: Fabrication and mechanical property analysis

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Abstract

Biocomposites derived from biodegradable materials can be an important tool for the development of a sustainable society. Composite materials composed of polylactic acid (PLA) and strong washi paper are expected to be a potential new class of materials although they have not yet been fully developed owing to the complexity of the compositing process. In this study, we attempted to composite PLA with washi paper under mild conditions by improving PLA–washi paper compatibility through PLA surface modification. By conducting photo-activated chlorine dioxide oxidation of the PLA surface, laminated PLA–washi paper composites were prepared via mild thermocompression bonding.

Introduction

To develop a sustainable society, it is important to replace fossil-based plastics with bio-based and biodegradable materials, including polylactic acid (PLA), polyhydroxyalkanoates, and starch-based polymers, and the related research fields are expanding.^[1–3] However, the practical use of these materials remains limited because of their lower mechanical strength and stability than those of conventional plastics. Composites of natural fibers and biodegradable polymers, known as green composites or biocomposites, are useful for various applications because these materials can be reinforced, while maintaining their environmental compatibility.^[4–10] Hotta et al. prepared a recycled-cellulose-nanofiber-reinforced PLA composite and reported that its Young's modulus reached as high as 1.84 GPa.^[11] In a different approach, Ohsawa et al. fabricated sheets of PLA reinforced with washi paper (Japanese traditional paper known for its high strength) and reported a 1.44-fold increase in tensile strength and 1.95-fold increase in Young's modulus in relation to those of pristine PLA sheets.^[12] However, the molding of these composites requires the melting and permeation of PLA between the fibers, which increases energy consumption and cost. Lamination is known to be an economical and effective method for preparing composite materials.^[13–15] However, the hydrophobicity of PLA and its weak adhesion to substrates are grave hindrances to the fabrication of laminated composites at low temperatures.

In a previous study, we developed an oxidative surface modification method for plastics using photo-activated chlorine dioxide (ClO_2^*).^[16–21] This method allows the cleavage of C–H bonds and the

introduction of oxygen functional groups on polymer surfaces.^[22] Accordingly, we achieved the functionalization of commodity plastics, such as polypropylene, imparting them with hydrophilic properties and adhesiveness to dissimilar materials.^[23] More recently, we applied this method to the surface modification of PLA and achieved the adhesive-free thermocompression bonding of modified PLA to aluminum and bacterial cellulose.^[24]

In this context, herein, we report mechanical strength improvement of the laminated composites of surface-modified PLA and washi paper using a photo-activated ClO_2^* gas treatment process to modify the PLA surface. In particular, we attempted to shorten the photo-oxidation treatment time and to composite the two materials at a low temperature (75 °C) in a short time (<1 min), aiming to develop a novel low-energy compositing process.

Experimental Section

Materials

PLA (Luminy L105) was obtained from Total Corbion. Washi paper (Junkouzo Paper, White, Ultrathin) was purchased from Inouekamiten. Sheets of washi with a thickness of 30 μm , a fiber diameter of 10–20 μm , and a density of 7.3 g/m^2 were used. The water content of the paper was evaluated by drying it in a vacuum oven at 105 $^{\circ}\text{C}$ for 2 h, and it was 6.1 wt%. The thickness was measured using a digital thickness gauge [CD-15AXW, Mitutoyo Corporation, Japan]. Sodium chlorite (NaClO_2) and toluidine blue O were obtained from Sigma-Aldrich. Hydrochloric acid (10 mol/L) was procured from FUJIFILM Wako Pure Chemical Corporation.

Preparation and modification of PLA films

Before use, PLA was re-precipitated by adding a chloroform solution of PLA to methanol. The precipitate was then separated and dried overnight. Thereafter, precipitated PLA was cast into a film by thermal pressing for 10 min under 10 MPa at 170 $^{\circ}\text{C}$. The thickness of the obtained PLA film was 135 ± 12 μm . The surface modification of the PLA film via photo-activated $\text{ClO}_2^{\bullet}$ gas treatment was performed as follows: all PLA films (1.3 cm $\times$ 6 cm for contact angle measurement and 3 cm $\times$ 6 cm for compositing) were washed with ethanol and dried in a vacuum oven at 25 $^{\circ}\text{C}$ before oxidation. The PLA film surface was oxidized using the photo-activated $\text{ClO}_2^{\bullet}$ gas generated by reacting a 20 mL aqueous solution of NaClO_2 (200 mg) and 10 M HCl aqueous solution (100 μL) upon UV irradiation (light-emitting diode lamp, $\lambda = 365$ nm, 5 mW/cm^2) in glassware covered with a glass plate; this allowed processing while separating the sample from the $\text{ClO}_2^{\bullet}$ aqueous solution.^[23] The reaction was conducted for different durations (10, 5, 1, and 0.5 min) at 30 $^{\circ}\text{C}$, and the oxidized samples were washed with distilled water and dried *in vacuo*. The samples treated for 10, 5, 1, and 0.5 min are designated as Ox-10, Ox-5.0, Ox-1.0, and Ox-0.5, respectively.

The plasma treatment of the PLA films was performed as follows: the film was treated for 1 min using vacuum plasma equipment (Sakigake Semiconductor, YHS-R). The plasma-treated samples

are designated as p-PLA.

Water contact angle measurement of PLA films

The static water contact angles of the PLA films were determined using a Drop Master DM300 contact angle meter (Kyowa Interface Science, Saitama, Japan). A 1.0 μL water droplet was placed on the PLA film surface, and the contact angle was measured immediately after the droplet contacted the PLA surface.

Preparation of PLA–paper composites

Composite specimens were prepared by layering washi paper and PLA films to form a three-layer PLA/washi/PLA structure, followed by hot pressing the structure using a compact heat press machine (H300-15, As ONE, Japan) at 75 °C and 10 MPa for 1 min. The prepared composites are designated as PLA sample name/w/PLA sample name. The thickness of the composites was around 300 μm for each of the specimens, with no significant difference shown. Since the PLA layer is larger than the washi paper layer, it is considered that the composites maintained a similar thickness regardless of the PLA type.

Tensile testing

Tensile tests were performed using a universal testing machine (EZ-S 10N, Shimadzu Co., Japan) with a 500 N load cell at a strain rate of 1 mm/min. Three samples from each group were analyzed, and the average value $\pm$ standard deviation is reported.

Cross-sectional observation

The cross-sections of the PLA/w/PLA specimens were examined through scanning electron microscopy (SEM; JSM-F100, JEOL, Japan) conducted at 5 kV. The specimens were fixed with epoxy resin (#15113 High Speed Epo; Konishi, Japan) and cut into cross-sectional specimens using a razor blade.

Biodegradability

The biodegradability of PLA/w composites (5 cm $\times$ 5 cm) was evaluated by placing them in

soil for 3 months. The specimens were retrieved every month, washed with distilled water to remove any adhering soil and dried under reduced pressure. The dry weights were then measured to assess the progress of biodegradation. Meteorological data were monitored at a weather station closet to the experimental field. Temperature and humidity for experimental period are shown in Table S1 and Figure S2.

Results and Discussion

Characterization of photo-activated-ClO₂[•]-oxidized PLA film

Water contact angle measurement was conducted to investigate the hydrophilicity of the PLA surface oxidized with photo-activated ClO₂[•] using an oxidation setup. As shown in Table 1, the untreated PLA film with a hydrophobic surface had a contact angle of $98^{\circ} \pm 0.7^{\circ}$, which decreased to $76^{\circ} \pm 3.7^{\circ}$ upon oxidation at 30 °C for 30 s, indicating that the surface hydrophilicity of the film was improved even within a short treatment time. Extending the treatment time improved the hydrophilicity further, and the water contact angle of the film (Ox-5.0) decreased to 60° after 5 min of oxidation. The hydrophilicity of this sample is comparable to that achieved after 60 s of plasma treatment, a conventional surface treatment process. However, the water contact angle increased slightly when the treatment time was extended to 10 min. This is possibly ascribable to the roughening of the PLA surface due to oxidation. In previous studies on the oxidative treatment of polypropylene, oxidation under high-temperature conditions or for long durations was found to lead to the roughening of the resin surface.^[17] In SEM images (Fig. S1), the untreated PLA film appears smooth, whereas the film oxidized for more than 10 min exhibits void-like structures and increased surface roughness.

Table 1. Water contact angles of PLA samples.

Samples	Reaction conditions		Water contact angle (°)
	Time (min)	Temperature (°C)	
PLA	—	—	98±0.7
p-PLA	1 min of plasma treatment		61±1.4
Ox-10	10	30	68±3.1
Ox-5.0	5	30	63±4.9
Ox-1.0	1	30	69±3.6
Ox-0.5	0.5	30	76±3.7

Mechanical properties of PLA–paper composites

The mechanical properties of the PLA–paper composites, such as strength, Young’s modulus, and elongation at break, were evaluated through tensile tests. Fig. 1(a) shows the typical tensile stress–strain curves of pristine PLA and the PLA/w/PLA composites, and the obtained mechanical parameters are summarized in Table 2. The strength of the untreated PLA–paper composite (PLA/w/PLA) was lower than that of the individual PLA film. The composite with the plasma-treated PLA films (p-PLA/w/p-PLA), which showed improved hydrophilicity, exhibited a lower strength than the PLA film. The strength and Young's modulus were also reduced for the Ox-10/w/Ox-10 composite obtained using PLA oxidized for a long time. This result is considered to be caused by damage to the PLA surface progressing with each treatment, leading to a decrease in the strength of the PLA at the interface with the washi-paper. In contrast, the composites of the PLA samples oxidized for shorter durations (1.0 and 0.5 min) exhibited excellent strength; the tensile strengths of Ox-1.0/w/Ox-1.0 and Ox-0.5/w/Ox-0.5 were 63.1 and 60.1 MPa, respectively, and their Young’s modulus were 3.21 and 3.19 GPa, respectively. Although the hydrophilicity values obtained from water contact angle measurements were not remarkable for these short time treated samples, it is interesting that the strength of each sample has been increased.

Fig. 1(b, c) shows the SEM images of a PLA–paper composite cross-sectioned with a razor blade after stabilization with epoxy resin. In the composite with untreated PLA, voids were observed between washi paper fibers and PLA, suggesting that the compatibility between the two materials was weak. In contrast, almost no voids were observed in the composite with oxidized PLA (Ox-0.5), indicating good compatibility. It should be noted that even the modification of only the top surface via rapid oxidation treatment can improve the PLA–washi paper compatibility and contribute to the increased mechanical strength of the composite. This enhanced compatibility is considered to result from interactions between carboxy groups introduced onto the PLA surface by oxidation and hydroxy groups in cellulose, similar to the adhesion between oxidized PLA and bacterial cellulose sheets

reported in our previous work.^[24] It is considered that hydrogen bonding between these dissimilar materials promotes interfacial composite formation, leading to enhanced mechanical properties.

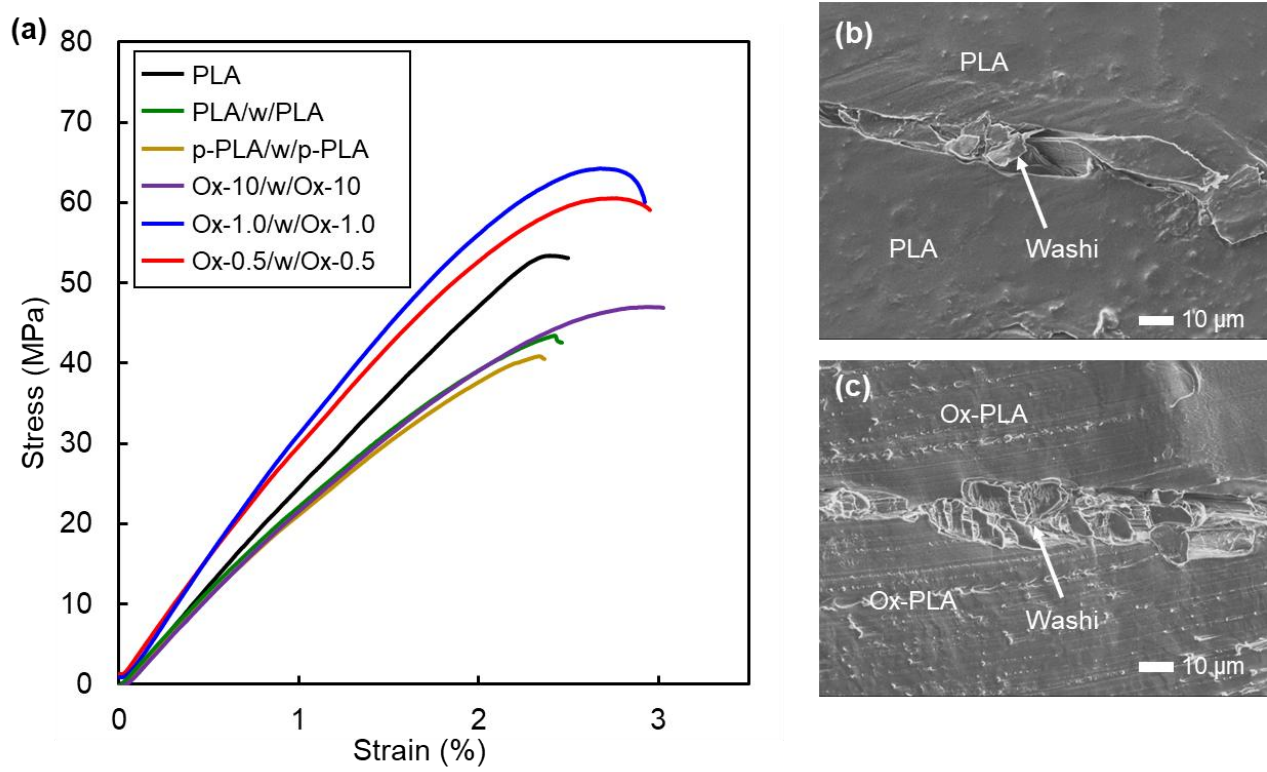


Figure 1. a) Typical stress–strain curves of untreated PLA and its composite with washi paper. Cross-sectional SEM image of the b) untreated PLA/w/untreated PLA composite and c) oxidized PLA/w/oxidized PLA composite.

Table 2. Mechanical properties of untreated PLA and the PLA/w/PLA composites.

Samples	Strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
PLA	53.3	2.47	2.35
PLA/w/PLA	47.6	2.35	2.49
p-PLA/w/p-PLA	49.5	2.21	2.38
Ox-10/w/Ox-10	47.0	2.18	2.85
Ox-1.0/w/Ox-1.0	63.1	3.21	2.58

Biodegradability

Fig. 2 shows the appearances of the untreated-PLA- and oxidized-PLA-based composites degraded in soil. No significant change is observed in the appearance of either sample. However, after 3 months in soil, yellowing, cracking and weight loss of several percentages were observed in both cases. Although sufficient degradation was not observed under these conditions, the behavior of oxidized PLA was similar to that of untreated PLA. For PLA alone, no weight loss was observed, and the samples did not yellow. This suggests that the presence of washi paper induces bacterial adhesion, possibly accelerating the degradation. Further detailed investigation is required on this point.

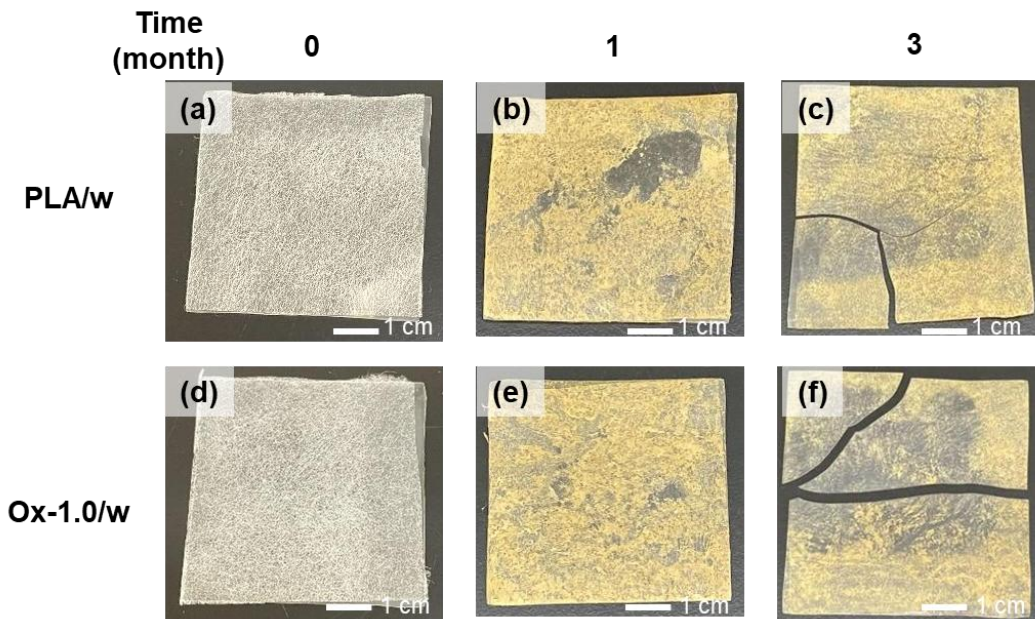


Figure 2. PLA/washi composite a) at the start of the experiment and after b) 1 month and c) 3 months in soil, oxidized PLA/washi composite d) at the start of the experiment and after e) 1 month and f) 3 months in soil.

Conclusion

In this study, we evaluated the effects of the surface modification of PLA on the properties of laminated PLA–washi paper composites. The strength of the composite with the surface-oxidized PLA film (63.1 MPa) increased by up to 1.3 times that of the untreated PLA film (47.6 MPa). Cross-sectional SEM images of the composites suggested that the surface oxidation of PLA enhanced its compatibility with washi paper. The time required to modify the PLA film surface was <1 min, and the composite of the PLA film with washi paper could be prepared under mild conditions (hot-pressing at 75 °C for 1 min). This fact suggests that photo-oxidative surface modification can serve as a novel method for preparing biocomposites, which may decrease energy consumption in relation to that achieved for the conventional composite preparation process. Although the biodegradability of the PLA-based composites must be investigated further and their degradation behavior in compost and water needs to be studied, their degradation characteristics are not expected to be significantly different from those of the individual pristine materials based on the results of this study. The results of this study are expected to expand the application scope of PLA-based composites and mitigate their environmental impact.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

H. A. designed the study and wrote the paper. N. O. and K. M. contributed to the experimental work. T. I. contributed to supervision and project administration.

Competing Interests

The corresponding author confirms on behalf of all authors that there are no financial or personal competing interests that would compromise the integrity of this manuscript.

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