Influence of water absorption on the fiber/matrix interfacial shear strength of glass fiber reinforced degradation controlled PLA model composite

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Abstract

Glass fiber reinforced plastics (GFRP) have many superior mechanical properties, such as high-specific strength and high-specific stiffness, and inexpensiveness compared with CFRP. Since the traditional matrix of GFRP such as epoxy, is not decomposed in the natural environment, polylactic acid (PLA), which is a plant-derived and biodegradable resin, has been receiving attention as an environmentally friendly material. Although good durability is required as in normal petroleum-based plastics when PLA is used for a matrix of FRP, PLA is expected to decompose quickly at the end of its lifetime. However, since the decomposition rate of PLA in the natural environment is very slow compared with other biodegradable resins, it is difficult to process a large amount of PLA in the natural environment. Recently, a method to control the rate of degradation of PLA has been developed by combining a decomposition accelerant and a degradation inhibitor with PLA. However, the influence of water absorption on the mechanical properties of PLA as the matrix of fiber reinforced composite materials has not been clarified yet. In this study, single fiber pull-out tests were conducted to clarify the influence of water absorption on the fiber/matrix interfacial shear strength of glass fiber reinforced degradation controlled PLA. The degradation inhibitor and the degradation accelerator are considered to suppress and accelerate the decomposition of PLA hydrolysis by water absorption respectively. The fiber/matrix interfacial shear strength of water absorbed specimens made with
PLA resin blended with degradation accelerator were almost the same as that of PLA. Although the fiber/matrix interfacial shear strength of the dry specimens made with PLA blended with degradation inhibitor was smaller than that of PLA, there is no reduction by water absorption for the specimens made with PLA blended with degradation inhibitor.

Keywords: PLA, glass fiber reinforced composites, water absorption, single fiber pull-out test, fiber/matrix interfacial strength, decomposition accelerator, degradation inhibitor.

1 Introduction

In the automotive industry, in order to follow carbon dioxide emission regulations, reducing vehicle weight is one of the important issues [1, 2]. Since glass fiber reinforced plastics (GFRP) have many superior mechanical properties such as high-specific strength and high-specific stiffness, and they are cheaper than carbon fiber reinforced plastics (CFRP), applications for mass-produced automobiles have been promoted. When thermosetting resins are used for the matrix of GFRP, however, recycling them is difficult and most parts are incinerated or landfilled instead of re-used or recycled [3, 4]. Under such circumstances, thermoplastic resins, particularly resins having biodegradability, which are excellent in recyclability have attracted attention. Poly lactic acid (PLA), which is plant-derived and biodegradable, has been getting attention as an environmentally friendly material. Thanks to price reduction by industrial mass production, the use of PLA is expanding [5]. However, in the natural environment, since the decomposition rate of PLA is very slow as compared with other biodegradable resins, it is difficult to process a large amount of PLA after their lifetime [6, 7]. In order to expand the use of PLA to mass-produced automobiles, it is necessary to have good durability as normal petroleum-based plastics when PLA is used for matrix of FRP, and it is also expected to be decomposed quickly at the end of its lifetime. Recently, a method to improve the control of the rate of degradation of PLA has been developed by combining a decomposition accelerator (PEOx: Polyethylene oxalate) and a degradation inhibitor (PMMA: Polymethyl methacrylate) with PLA [8, 9]. When PLA is combined with the decomposition inhibitor, it is possible to suppress hydrolysis by water absorption in contact with the water in use. On the other hand, at the time of disposal, by exposing it to a high-temperature environment with the addition of an enzyme, the surface of PLA is decomposed by water and an enzyme that are the triggers of the decomposition; then the acid is released by hydrolysis, and the degradation rate is drastically increased by hydrolysis of PLA that is accelerated by the released acid. Although the properties of the resins have become clear, the composite materials are not clarified yet [10], it is necessary to evaluate the composite mechanical properties of glass fiber reinforced PLA is combined PMMA and PEOx in consideration of the water environment for automotive applications. The mechanical properties of GFRP are affected not only by reinforced fibers and matrix resins, but also particularly by the fiber/matrix interface [11]. In this
study, the influences of water absorption on the fiber/matrix interfacial shear strength of glass fiber reinforced PLA resin, PLA resin blended with decomposition accelerator of 5 wt%, PLA resin blended with degradation inhibitor of 5 wt%, PLA resin blended with degradation inhibitor of 30 wt%, and PLA resin blended with decomposition accelerator of 4 wt% and degradation inhibitor of 1 wt% was clarified by using a single fiber pull-out test.

2 Materials and experimental method

2.1 Materials

Following five types of PLA were used as matrix: neat PLA resin (poly lactic acid, Zhejiang Hisun Biomaterials), PLA resin blended with decomposition accelerator (PEOx: Polyethylene oxalate) 5 wt% (deg-PLA), PLA resin blended with degradation inhibitor (PMMA: Polymethyl methacrylate) 5 wt% (PLA+PMMA (5)), PLA resin blended with degradation inhibitor 30 wt% (PLA+PMMA (30)), and PLA resin blended with decomposition accelerator 4 wt% and degradation inhibitor 1 wt% (deg-PLA+PMMA). Plain woven glass fiber (Nitto Boseki Co., Ltd) of 203 g/m² was used for reinforcement.

2.2 Water absorption test

A water absorption test was conducted in a 100% relative humidity environment in order to evaluate the weight gain due to water absorption and the weight loss due to elution on the five types of PLA. Specimens were cut into a rectangular shape (25 mm × 40 mm × 2 mm) were maintained at 80°C for 1 hour using a constant temperature oven under 100% relative humidity environment. Then the weight W of the specimens were measured using the electronic balance after wiping the surface of the specimens. Weight gain rate (M) was calculated using eqn (1). 1 h water absorbed specimens will be called “wet specimen”.

\[ M = \frac{W - W_0}{W_0} \times 100 \]  

where \( W \) is the specimen’s weight after water absorption test of 1 hour, and \( W_0 \) is the specimen’s weight before water absorption.

After the water absorption tests, some specimens were maintained at 80°C for 1 hour using a constant temperature oven under 0% humidity environment. These are denoted as, ‘Re-dried specimens’. The water absorption rate (\( M_a \)) and the weight loss rate (\( M_l \)) were calculated using eqns (2) and (3).

\[ M_a = \frac{W - W_d}{W_0} \times 100 \]  

\[ M_l = \frac{W_d - W}{W_0} \times 100 \]
where $W_d$ is the re-dried specimen’s weight.

Figure 1 shows the relationship of weight gain, weight loss and water absorption.

![Figure 1: Relationship of weight gain, weight loss and water absorption.](image)

### 2.3 Single fiber pull-out test

In order to evaluate the influence of water absorption on the fiber/matrix interfacial shear strength, single fiber pull-out tests were conducted.

The five types of resins described in section 2.1 were used for the matrix of the specimens. Figure 2 shows a schematic drawing of the preparation for a pull-out specimen. After a single fiber was glued to the tab with adhesive, the tab was attached to a micromanipulator. The resin was placed using the micromanipulator on the aluminum plate which was heated at molding temperature, and the single fiber was embedded to the matrix.

Some specimens were kept in the same conditions of the water absorption test of resins to prepare water absorbed specimens (will be referred to “wet”) and some water absorbed specimens were dried to prepare re-dried specimens (will be referred to “Re”) as described in section 2.2. Pull-out tests were performed for dry, water absorbed and re-dried specimens for GF/PLA, GF/deg-PLA, GF/PLA+PMMA (5), GF/PLA+PMMA (30) and GF/deg-PLA+PMMA model composites.
Figure 2: Preparation of pull-out specimen.

After chucking specimen with a pin hole in the tab, the supporting part of the tab was cut and the pull-out test was conducted using a constant displacement rate of $1.67 \times 10^{-6}$ mm/sec (0.1 mm/min) by the Micro Material Testing Machine (MMT-11N, Shimadzu Corp. Japan). For the calculation of the interfacial strength, the cross-section area of each fiber was measured by scanning electron microscope (SEM, JSM-6390LT, JEOL Ltd, Japan) after each pull-out test. The interfacial shear strength, $\tau$, was calculated with eqn (4).

$$\tau = \frac{F_{\text{max}}}{\pi dl}$$

where $F_{\text{max}}$ is the maximum load in the pull-out test, $d$ is a fiber diameter and $l$ is an embedded length measured by SEM.

3 Results and discussion

3.1 Water absorption test

Figure 3 shows the relationship between weight gain, weight loss and water absorption of the resins.

The weight gain rates of PLA and deg-PLA were 0.2% and 1.4%, respectively, and water absorption rates were 0.8% and 4.4%, respectively. Both the water absorption rate and weight gain rate of deg-PLA were found to be higher than those of PLA. The weight loss rate was considered to be caused by hydrolysis, and the degradation accelerator PEOx can be considered to accelerate the decomposition of PLA hydrolysis. PLA and deg-PLA were 0.6% and 3.1%, respectively. The weight loss rate of deg-PLA+PMMA was 0.3%, which was lower than that of PLA (0.6%). The weight loss rate of PLA+PMMA (5) was 0.2% and the weight loss rate of PLA+PMMA (30) was 0.0%, which were lower than that of PLA (0.6%). The degradation inhibitor, PMMA can be considered to suppress the hydrolysis of PLA and inhibit the weight loss.
Figure 3: Water absorption test.
3.2 Single fiber pull-out test

Figure 4 shows the fiber/matrix interfacial shear strength of model composites obtained by single fiber pull-out tests.

(a) Water absorption on degradation inhibitor PLA

(b) Water absorption on degradation accelerator PLA

Figure 4: Interfacial shear strength.
The interfacial shear strength of the wet specimens (1h) of GF/PLA, GF/deg-PLA, GF/PLA+PMMA (5), GF/PLA+PMMA (30), and GF/deg-PLA+PMMA were decreased by 64%, 63%, 10%, 33%, and 34%, respectively, compared with each dry specimen. The fiber/matrix interfacial shear strength of 1h water absorbed specimens made with PLA resin blended with degradation accelerator were almost same as that of PLA. On the re-dried treatment, although only the strength of GF/PLA+PMMA (30) had recovered the strength level of the dry specimens, the strength of re-dried specimens is almost same as the wet specimens or smaller than that of wet specimens. Therefore, the reduction of interfacial shear strength by water absorption of GF/PLA, GF/deg-PLA, GF/PLA+PMMA (5), GF/deg-PLA+PMMA is considered to be due to chemical deterioration owing to hydrolysis of the resins. Since the interfacial shear strength of the re-dried specimens of GF/PLA+PMMA (30) has been regained comparing with that of the wet specimens, hydrolysis can be suppressed by the blending of the 30% of PMMA. Considering the fact that the interfacial shear strength of re-dried specimens of GF/deg-PLA was smaller than the wet specimens, absorbed moisture after water absorption and dry treatment at 80°C may cause hydrolysis of the resin in deg-PLA during the dry treatment. Although the fiber/matrix interfacial shear strength of the dry specimens made with PLA resin blended with degradation inhibitor was smaller than that of PLA, there is no reduction by water absorption for the specimens made with PLA blended with degradation inhibitor.

4 Conclusions

The influences of water absorption on the fiber/matrix interfacial shear strength of glass fiber reinforced PLA resin, PLA resin blended with decomposition accelerator of 5 wt%, PLA resin blended with degradation inhibitor of 5 wt%, PLA resin blended with degradation inhibitor of 30 wt%, and PLA resin blended with decomposition accelerator of 4 wt% and degradation inhibitor of 1 wt% were clarified by using a single fiber pull-out test. The investigation yielded the following conclusions:

(1) The degradation inhibitor, PMMA, and the degradation accelerator, PEOx are considered to suppress and accelerate the decomposition of PLA hydrolysis by water absorption respectively.

(2) The fiber/matrix interfacial shear strength of 1h water absorbed specimens made with PLA resin blended with degradation accelerator were almost same as that of PLA.

(3) Although the fiber/matrix interfacial shear strength of the dry specimens made with PLA resin blended with degradation inhibitor was smaller than that of PLA, there is no reduction by water absorption for the specimens made with PLA blended with degradation inhibitor.

(4) Although the fiber/matrix interfacial shear strength of 1h water absorbed specimens for PLA resin blended with degradation inhibitor 30 wt% was smaller than that of dry specimens, their re-dried specimens has the strength level of the dry specimens.
References


