Effect of Surface Treatment on Interfacial Strength between Bamboo Fiber and PP Resin*

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The interfacial shear strength (IFSS) between a bamboo fiber bundle and maleic anhydride polypropylene (MAPP) was examined for various kinds of surface treatments in conjunction with ultrasonic washing. Bamboo fiber bundles were extracted from Chinese bamboo by either mechanical scratching or steam explosion. The effect of fiber bundle diameter on IFSS was measured by using the micro-droplet test. The test results showed that higher IFSS was observed for bundles having smaller diameter. Isocyanate silane treatment improved IFSS in the case of raw bamboo fibers while it was less effective to improve IFSS for steam exploded fibers. The highest tensile strength of bamboo fiber reinforced polypropylene was obtained when steam exploded bamboo fibers were used as the reinforcement.

Key Words: Bamboo Fibers, Surface Treatment, Green Composites, Interfacial Shear Strength, Polypropylene

1. Introduction

One of the environmental problems on the earth is the “Green house” problem. This environmental problem is extremely serious in 21 Century. Fossil oil based polymer composites yield carbon dioxide gas when the materials are scrapped and burned. Therefore, bioplastics and natural plant fibers are focused and being developed as future eco and green materials, eliminating some environmental problems connecting to the waste.

Bamboo, with a maturation period of 3–8 years, grows more rapidly than any other woods on the earth as long as the authors know. Bamboo can yield cellulose per acre 2–6 times as much as pine under the optimum condition⁽¹⁾, so that some researchers have tried to find their industrial applications. One of applications of bamboo as industrial resources is fiber. We successively extracted thin bamboo fiber bundles*¹ (referred shortly as bamboo fibers) from raw bamboo by using the steam explosion method⁽²⁾, consisting of several ten to a hundred monofilaments. Their mechanical properties are as superior as those of glass fibers. Bamboo fibers could be used as reinforcement for some polymer matrices instead

of glass fibers.

The interfacial strength between fiber and matrix has a strong effect on the strength of composites. Bamboo fibers consist of cellulose, hemi-cellulose and lignin. Lignin is hydrophobic. That is, we cannot expect strong adhesion with many polymers, and the interfacial strength is resultantly low between bamboo fiber and some conventional matrix resins. Therefore, the surface condition of bamboo fiber is very important while some reports have been published concerning with surface modification of natural fibers to improve the interfacial strength between natural fibers and conventional matrices, both thermoplastics and thermoset resins.

The objective of the present work is to examine the effect of surface treatment on the interfacial strength between bamboo fiber and PP (polypropylene) matrix due to silane coupling agents. We used the micro-droplet test to identify the interfacial strength between bamboo fiber

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^{*1} Single fibers (monofilaments) exist in bamboo, and we can extract single fibers (monofilaments) from raw bamboo by chemical treatment, whose diameter is 10 to 35 μm at largest. They are known as bamboo pulp, but not long enough to spin into yarn. They are also strongly bent and not strong enough to reinforce polymers due to chemical treatment. Monofilaments are strongly adhered with each other to form a fiber bundle with lignin and hemi-cellulose. Therefore, it is difficult to extract very thin, but long fiber bundles without giving serious damage to them by physical processing as well as obtaining single fibers.

and maleic grafted polypropylene (MAPP) before and after treating fibers with some silane coupling agents.

2. Experiment

2.1 Materials

We used two types of Chinese bamboo fibers. The first type was imported from China. The diameter of bamboo fibers was about 100–450 μm . These fibers were mechanically extracted. They are designated as raw bamboo fibers.

The second type of fiber was extracted by the steam explosion method. In this method, some strips of Chinese bamboo grown in our campus were placed into an autoclave. The bamboo strips were steamed with overheated steam in the autoclave. The temperature was kept at 175°C and the pressure at 0.8 MPa. Then, the steam pressure was suddenly released to the atmosphere. Micro steam explosions occurred in many soft cells, and the cell walls of bamboo were cracked. The above process was repeated 9 times to assure that all cell walls had been cracked. At elevated temperature, some compositions of bamboo decompose, and bamboo becomes soft enough to extract fibers. They are referred as steam exploded fibers.

In order to promote a massive use of bamboo fibers, bamboo fibers should be applied to reinforce thermoplastics such as polypropylene (PP) as a material for injection molding. However, PP is hydrophobic. Generally, the adhesion of PP with respect to fibers are poor. Therefore, we used 5% Maleic Anhydride grafted Polypropylene (MAPP) as the matrix of green composites.

2.2 Surface treatments

In this study, we used isocyanate silane, amino silane and methacryloxy silane (supplied by Sinetsu Silicon Co., Ltd.) in an attempt to improve the surface of bamboo fibers. Bamboo fibers were treated in each silane solution for 5 min. Then, bamboo fibers were dried in an electric oven at 150°C for 1 hour.

2.3 Micro-droplet tests

Micro-droplet tests were carried out by using a composite interface testing machine (HM410: Touei Industry Co., Ltd.) (see Fig. 1). Tests were conducted under the laboratory condition: $21 \pm 3^\circ\text{C}$ and $60 \pm 5\%$ RH. The tensile speed was 0.5 mm/min.

Fig. 1 Schematic drawing of micro-droplet testing and a fiber sample

The interfacial shear strength (IFSS) is calculated by the following equation⁽³⁾:

$$IFSS = F_p / (L_1 - L_2)$$

Here, F_p is the maximum load to pull out the fiber from the matrix. L_1 is the embedded length of the fiber. L_2 is the circumference of the fiber.

3. Results and Discussion

3.1 Bamboo fiber structure

The primary compositions of bamboo fiber are cellulose, hemi-cellulose and lignin as before mentioned. Their ratio is about 2 : 1 : 1. A single bamboo fiber (monofilament) consists of four layers⁽⁴⁾, where crystallized cellulose microfibrils (MFC) are longitudinally aligned with some small angles with respect to the fiber axis except the top (P) layer (Fig. 2). MFCs are bonded together with hemi-cellulose and lignin. Lignin plays an important role in formation of fibers as matrix while MFCs plays as reinforcement. Hydrophilic cellulose and hemi-cellulose exist on the surface of bamboo fibers, but they are also covered with hydrophobic lignin⁽⁵⁾. We cannot expect strong adhesion between lignin and MAPP so that an appropriate surface treatment is obliged.

Steam exploded bamboo fibers are also mechanically separated from steam exploded bamboo strips at the final stage. It is difficult to supply fibers having almost the same dimensions and configuration (diameter, aspect ratio and shape of cross section). Figure 3 shows the cross sections of some bamboo fiber bundles. The diameter of a single (Chinese) bamboo fiber (monofilament) is about 10–20 μm but its length is about 1–2 mm. It is necessary for us to remember that no single fibers longer than 10 mm exist in bamboo. On the other hand, long fibers can be extracted from cotton and many grasses such as jute and flax. Therefore, we have to utilize thin fiber bundles of bamboo as the reinforcement of PP matrix. (a) is a typical cross section of a fiber bundle whose diameter is smaller than others. A cluster of single fibers is distinguishable without soft cells surrounding the cluster. On the other hand, in the case of a large fiber bundle, some soft cells sticking onto the outer edge of the fiber bundle exist. A piece of another bundle also sticks (b). In the case of a steam exploded bamboo fiber bundle, crushed soft cell walls are found sticking onto the cluster edge (c).

Fig. 2 Micro-structure of a single bamboo fiber

Fig. 3 Cross sections of bamboo fiber bundle

3.2 Effect of silane coupling agent on IFSS

The surface of bamboo fibers is very important to achieve high IFSS. Among three primary compositions of bamboo fiber, cellulose has a good adhesion with hydrophilic matrices. However, it is difficult to extract bamboo fibers (bundles) whose surface is covered with almost cellulose. That is why we try to modify bamboo fiber surface to improve the adhesion with respect to matrices.

Bamboo fibers were firstly treated with three different silane coupling agents of 2% concentration while thin raw fibers as small as 0.1–0.15 mm in diameter were used, which had been carefully selected. The test results for IFSS are given in Fig. 4. In the case of isocyanate silane, IFSS increases about 10% in comparison with the untreated case. Amino silane also increases IFSS between bamboo fiber and MAPP while methacryloxy silane reduces IFSS lower than the untreated case. During the surface treatment process, bamboo fibers adsorbed silane

Fig. 4 Effect of different silane treatment on IFSS for raw bamboo fibers

solution. Amino- and isocyanate silanes contain amino (NH_2) and cyanua groups (CN). These groups enhance the interaction between coupling agent and cellulose in bamboo fibers. Our results agree with the results given by Belgacem, M.N., et al.⁽³⁾ In addition, there is a hydro-bond between amino group and OH^- group in cellulose. These mechanisms explain why amino and isocyanate silanes have more influence on IFSS than other treatments. Therefore, we will use only isocyanate silane for further experiments.

3.3 Effect of fiber bundle diameter on IFSS

Figure 5 shows the relationship between IFSS and fiber bundle diameter for both untreated and isocyanate silane treated fibers. IFSS between bamboo fiber and MAPP decreases as the fiber bundle diameter increases. According to Moom, C.K.⁽⁶⁾, this tendency is attributed to shrinkage of resin during consolidation in the case of thermoset-plastics based composites. Even for thermoplastics (TP) based composites, the mechanism similar to thermoset composites acts due to thermal shrinkage of TP resin after injection molding. As the fiber bundle diameter increases, the shape of fiber cross section becomes complex. Imperfect contact between TP resin and bamboo fibers occurs at many locations on the fiber surface due to voids derived from the complex geometry of fiber surface, which causes the reduction of IFSS in spite of the appropriate surface treatment (isocyanate silane). As can be seen in Fig. 7 (b), unexpected soft cells increase, whose shear strength is much lower than that of hard fiber surface. Resultantly, the observed shear strength given as an average value decreases with an increase of fiber diameter.

In the case of steam exploded bamboo fibers, we obtained a similar result for the relationship between IFSS and fiber bundle diameter as can be seen in Fig. 6. IFSS decreases with increasing the bundle diameter. However, the difference in IFSS between treated and untreated fibers is not distinguishable while it is much significant in the case of raw bamboo fibers. In addition, IFSS of steam exploded fibers is higher than that of raw bamboo fibers

Fig. 5 Effect of diameter on IFSS (raw fibers)

Fig. 6 Effect of fiber bundle diameter on IFSS (steam exploded bamboo fiber)

(a) Raw fiber

(b) Steam exploded

Fig. 7 SEM micrographs showing bamboo fiber bundle surface

for the same diameter. This result indicates that some lignin covering the surface might have been partially decomposed due to high temperature steam during the steam

Fig. 8 Effect of ultrasonic washing on IFSS

Fig. 9 Relation between IFSS and silane concentration (raw fibers)

explosion process.

However, there still exist many soft cells sticking onto the bamboo fiber surface, which have less shear resistance. In order to remove those unexpected cells from steam exploded fibers, they were washed under ultrasonic sound. After washing, the fibers were treated with isocyanate silane. The micro-droplet test results are given in Fig. 8.

After washing, IFSS changed a little, but not significant. Ultrasonic sound may have helped to remove some cells (refuse) from bamboo surface. Still some refuse sticks to the surface, so that the bonding between bamboo fiber and matrix is not satisfactory. Less improvement was obtained in IFSS even if fibers were treated with isocyanate silane after ultrasonic washing.

3.4 Effect of silane concentration on IFSS

The effect of isocyanate silane concentration on IFSS of raw bamboo fibers was examined. The test results are given in Fig. 9. When increasing concentration of silane from 0.5% to 1%, an increase of IFSS is appreciated, especially for fibers of which diameter is smaller than 0.4 mm. However, the difference between 1% and 2% is not distinguishable.

The silane agent firstly meets the fiber surface. The

groups of silane interact with cellulose partially exposed on the fiber surface. With increasing silane concentration, more silane groups contact with bamboo fibers and the surface is more activated. However, the absorption on the fiber surface is limited and saturated. Excessive silane agent does not improve the surface activation. 1% concentration is enough to cover the all surface of bamboo fibers. As previously mentioned, the total amount of unexpected soft cells increases as the diameter of bamboo fiber bundles increases. Even if the bamboo fiber surface including soft cells is well improved due to the silane coupling agent, IFSS measured by the micro droplet test does not increase since the shear failure occurs between damaged soft cell(s) and the solid surface of bamboo fibers. Therefore, 0.5% silane concentration is enough to obtain the strong bonding between MAPP matrix and soft cell walls for thick bundles. In addition, the strength between MAPP and soft cell walls is enough to cause the interfacial failure between soft cells and the solid surface of bamboo fibers even in the case of no treatment.

3.5 Tensile strength of BFPP

BFPP (Bamboo Fiber reinforced Polypropylene) was fabricated using MAPP thin film and bamboo fibers. First, short bamboo fibers (0.2–0.3 mm in diameter and 10–30 mm in length) are dispersed on a MAPP sheet, then, several sheets are alternatively stacked. Finally, they are hot pressed at 190°C under the pressure of 2 MPa. The variation of tensile strength of those BFPP (fiber fraction: about 30 wt%) is shown in Fig. 10. From this figure, we understand BFPP using steam exploded bamboo fibers with no treatment has the highest strength. It also shows the silane treatment improves the tensile strength of BFPP in the case of raw bamboo fibers, but it has no effect on the tensile strength for steam exploded bamboo fibers. This result is consistent with the IFSS test results shown in Fig. 6, where no silane effects exist for the steam exploded fibers.

4. Conclusions

1. Isocyanate silane and amino silane coupling agents improve the interfacial adhesion between a raw bamboo fiber and MAPP matrix.
2. 1% concentration of Isocyanate silane is enough to

Fig. 10 Tensile strength of BFPP

improve IFSS for raw bamboo fibers.

3. Isocyanate silane treatment has little effect on the improvement of IFSS (interfacial shear strength) between a steam exploded bamboo fiber and MAPP matrix.

4. As the fiber bundle diameter increases, IFSS decreases.

5. Steam exploded fibers are appropriate for BFPP. No surface treatments are necessary.

References

- (1) Chen, C.-M., Chen, H.-C., Tracy, M. and Liao, Y., Bonding Moso Bamboo with Copolymer Resins Made of Biomass Residue Extracts with Phenol and Formaldehyde, *Forest Products Journal*, Vol.50, No.9 (2000), pp.70–74.
- (2) Fujii, T., Okubo, K. and Shito, T., *J. of Fiber Science Soc.*, Vol.59, No.3 (2003), pp.84–88.
- (3) Miller, B., Muri, P. and Rebenfeld, P., A Microbond Method for Determination of the Shear Strength of a Fiber/Resin Interface, *Composites Sci. and Tech.*, Vol.28 (1987), pp.17–32.
- (4) Secondary Xylem Formation — Introduction to Biomass Science, edited by Fukushima, K., Funada, R., Sugiyama, J., Takebe, K., Umezawa, T. and Yamamoto, H., (2003), p.65, Kaiseisha Press.
- (5) Jain, S., Kumar, R. and Jindal, U.C., Mechanical Behaviours of Bamboo and Bamboo Composite, *J. Mate. Sci.*, Vol.27 (1992), pp.4598–4604.
- (6) Moom, C.K., Lee, J., Cho, H.H. and Kim, K.S., Effect of Diameter and Surface Treatment of Fiber on Interfacial Shear Strength in Glass Fiber/Epoxy and HDPE, *J. Applied Polymer Sci.*, Vol.45 (1995), pp.443–450.