TENSILE PROPERTIES OF WASHI-PAPER REINFORCED POLYLACTIC ACID (PLA) AS A GREEN COMPOSITE

I.Ohsawa, J.Takahashi, K.Uzawa, M.Kanai, H.Murayama, K.Kageyama
Department of Environmental and Ocean Engineering, The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, ohsawa@giso.t.u-tokyo.ac.jp

ABSTRACT

Bio-degradable plastics of plant-based and carbon neutral are the focus of attention in recent years from the view point of global environmental concerns. In such a background, this study investigated the mechanical tensile properties of green composites, namely “Washi-paper” reinforced polylactic acid (PLA). Washi is a traditional Japanese paper which is used in various purposes in our life. Recently a new type of Washi-paper, which is not easy to tear and has high strength, has been developed and manufactured. Also, the fiber length of Washi is relatively long compared to commonly used Yoo-shi (western-style paper). In addition, the dispersion in paper quality is small and high quality stable Washi-paper can be obtained as one layer of composite laminates. In this research, the tensile properties of Washi-paper are examined first. Next, Washi paper is moulded with PLA resin and the tensile properties of the green composites are evaluated using the rule of mixtures.

KEY WORDS: Washi-paper, PLA, Tensile properties, Green composite

1. INTRODUCTION

In recent years, industries are developing and manufacturing “greener” materials, the government is encouraging bio-based product research, and the people are realizing the value of environmentally friendly products1). On the other hand, glass-fiber reinforced plastics (GFRP) and carbon-fiber reinforced plastics (CFRP), which use oil-based plastics, are the mainstream in the field of fiber reinforced plastics. Hence, establishment of the system of disposal and recycling becomes a problem. Though the bio-composite, that is, the combined plant-based resin and fiber, does not reach the strength and the Young’s modulus of conventional composite, the bio-composite can maintain a certain level of strength and rigidity2), it has a low price, and it can be naturally reproduced. In addition, its negative environmental impact in the disposal process is small. The usage of the FRP called "Green composite" is being extended to the automotive industry also1).

Washi-paper can be seen in shoji and sliding doors in our house from olden days. As for “paper mulberry” which is the main raw material for Washi-paper, a lot of paper mulberries are grown in various places in Japan as cultivation is easy. As the fiber is long3), it has a variety of uses. The strength of the Washi-paper depends on raw materials and the processing method. Paper made of long-fiber is called Washi-paper, and paper made of short-fiber is called Yoo-shi (Western-style paper). In case of the western-style paper, short fibers obtained from conifer trees and broadleaf trees, are the main materials and the length of the fiber is 4.5 mm or less3). But in the case of Washi-paper, long fibers obtained from the bast fiber and leaf fiber are main materials, and the length of the fiber is 50 mm maximum. Its specific gravity is 0.39, that is, less than half compared with the specific gravity of 1.0 of western-style paper, it is also flexible, not easy to tear and has high strength. In addition, preservation of
Washi-paper is excellent because of its alkalinity or neutrality. However, its demand is decreasing in recent years because of westernization of houses, and new development of Washi is demanded.

PLA is a bio-plastic obtained from lactic acid fermented from the starch of plants such as corn and potatoes, and is manufactured using polymer technology. Moreover, it is a bio-degradable plastic resolves to water and carbon dioxide \((\text{CO}_2)\) by an underground microorganism when disposing it, and it is friendly to the environment since the poisonous substance is not generated even if it burns, and the generation of calories when incinerated is low compared with other plastics, it does not hurt the incinerator. However, cost of the PLA was a big problem because it was priced 5-10 times that of general-purpose plastic, which hinders its spread. But a major chemical company in the United States began production on a large scale in recent years. Then, it is thought that the cost of PLA will decrease.

### 2. Materials

Polylactic acid (PLA) resin pellet LACEA H-100\(^3\) made by Mitsui Chemicals Ltd. (shown in Fig.1) (164 degree Celsius in melting point : \(\rho=1.26\)) was used. This PLA resin is classified as a hard resin. Five kinds of Washi-paper were obtained from the Japanese paper as given below (catalog description). The weight per unit area and thickness of each Washi-paper are shown in Table 1. Fig.2 shows one example of Japanese paper.

<table>
<thead>
<tr>
<th></th>
<th>Thickness (mm)</th>
<th>Weight (gram/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Washi-paper A</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>Washi-paper B</td>
<td>0.16</td>
</tr>
<tr>
<td>3</td>
<td>Washi-paper C</td>
<td>0.13</td>
</tr>
<tr>
<td>4</td>
<td>Washi-paper D</td>
<td>0.13</td>
</tr>
<tr>
<td>5</td>
<td>Washi-paper E</td>
<td>0.18</td>
</tr>
</tbody>
</table>

*Table 1 Five kinds of Washi-paper*

1) Washi-paper A: (It does not slacken easily, super-strong quintuple & pure-white solid color)
2) Washi-paper B: (Perfect solid color. Strength is 4.5 times that of general shoji paper)
3) Washi-paper C: (Tosa-Washi that contains 100% paper mulberry without fluorescence)
4) Washi-paper D: (The solid color. Strength is 3.5 times that of general shoji paper, 60% paper mulberry and 20% Manila hemp)
5) Washi-paper E: (Special heat bonding resin, UV resistance processing, 50% pulp, 20% hemp, and 30% rayon/polyester/vinylon binder)

Currently, various kinds of Washi-paper are available according to the manufacturing method, fiber element, etc. A little plastic binder is added to bonding the fiber as stated above, to make the paper strong.

![Fig. 1 PLA pellet](image1)

![Fig. 2 Japanese paper “Washi”](image2)
3. Molding and tensile specimens of Washi-paper/PLA composites

The molding know-how using a hot press machine can be accumulated in the laboratory, and composite materials with few voids can be molded. The detailed procedure is shown below.

1) A thin sheet of about 0.3mm thickness without voids is made with PLA dried pellet using a hot press. Pressure is 2 MPa, and temperature is 180 degree Celsius.
2) The aluminum metal mold is prepared with which a board of 1-mm thickness, 130-mm width, and 160-mm length can be molded.
3) PLA thin sheet with the dried Washi-paper is prepared and cut out.
4) The PLA sheet and Washi-paper are alternately placed in a metal mold. The voids are removed by repeated pressurizing/decompression at 0 MPa to 5 MPa at 180 degree Celsius. Afterwards, it is maintained at 5 MPa for several minutes.
5) The thickness of the specimen board is fixed at 1 mm, and the molded composite may consist of one Washi-paper layer, two paper layers, and three layers respectively.
6) The resin was cooled quickly, and molded promptly without crystallization.

Figure 3 shows an extremely transparent, thin sheet of non-crystal molded from PLA pellet. Figure 4 shows a tensile composite specimen reinforced with three layers Washi-paper.

4. Tensile experiment results and the discussion

4-1 Tensile examination of Washi-paper

Figure 5 shows a view of the experiment. Waterproof sandpaper #600 was used for reinforcement of the gripping chuck of the Washi-paper. A paper specimen was from a strip of Washi-paper of 15 mm in width and 150 mm in the total length. Length between the gripping chucks was 90 mm. Figure 6 indicates the relation between load and time for 0- and 90- degrees direction of Washi-paper C (Tosa-washi) as one example. Because the expansion could not be measured directly with extensometer, tensile strain was converted based on the amount of movement between the gripping chucks. Since the tensile speed is 1 mm/min, 60 seconds of loading (horizontal axis) correspond to 1.1% strain apparently. Because the real thickness of the paper is indefinite, the load value is shown on the vertical axis of Fig. 5. The difference in the characteristics of five kinds of Washi-paper in the 0- and 90-degrees direction is clear. Moreover, large differences in the directionality of characteristics of machine-made paper were found compared to handmade paper. The reproducibility of experimental data was extremely good.
Figure 7 is a line chart displayed together in the 0-degree direction of good strength for five kinds of Washi-paper. A noticeable characteristic difference was confirmed, according to the kind of Washi-paper. Especially, unexpected results were obtained with an expansion of as much as 24% shown in “Washi-paper B”. The compound material made with PLA described later was tried by using “Washi-paper E” that endured the highest load among the five kinds of papers.

4-2 Tensile examination of PLA
In Figure 8, the stress-strain diagram of PLA tensile examination is shown. The thickness of the specimen is 0.3mm, and the length and width are equal to those mentioned above. The mean values of five results are shown in Table 2, and the data showed little difference. It was observed that the degree of elasticity increased slightly in the specimen for the resin cooled slowly and crystallizes when forming, and the elongation and strength decreased instead.
Data shows mean values of five specimens

Table 2 Mean values of tensile test of non-crystallized and crystallized PLA

<table>
<thead>
<tr>
<th>Vf of Washi</th>
<th>Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Young’s M (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 (1 layer)</td>
<td>43.1</td>
<td>1.20</td>
<td>4.16</td>
</tr>
<tr>
<td>15.4 (2 layers)</td>
<td>64.9</td>
<td>1.76</td>
<td>5.12</td>
</tr>
<tr>
<td>21.8 (3 layers)</td>
<td>68.6</td>
<td>1.52</td>
<td>6.20</td>
</tr>
</tbody>
</table>

![Stress-strain diagram of PLA tensile test](image1)

**4-3 Tensile examination of Washi-paper/PLA composite**

The composite was molded with high strength “Washi-paper E” using non-crystalline PLA. The thickness of the specimen was fixed at 1mm, and “Washi-paper E” was molded with 1 layer, 2 layers, and 3 layers. The volume fraction (Vf%) of the Washi-paper was 8.1%, 15.4%, and 21.8% respectively. This Vf value was calculated from the value of the weight of paper/PLA composite, the weight of Washi-paper, and the specific gravity of PLA. Figure 9 shows a typical stress-strain diagram of the composite with one Washi-layer, two layers, three layers, and the non-crystalline PLA. Table 3 and Fig.10 show the mean value of every five specimens. It is seen that both strength and the Young’s modulus improve by making a composite with Washi-paper. The Young’s modulus has increased 1.95 times especially for three layers compared with PLA, and strength has improved 1.44 times.

![A typical stress-strain diagram of Washi/PLA composites](image2)

![Relation between Young’s modulus and volume fraction of Washi-paper for Washi/PLA composites](image3)
4-4 Young’s modulus comparison with Kenaf/PLA composite

Young’s modulus in tension of uni-directional Kenaf/PLA composite was obtained from the experimental data as 16.6 GPa\(^5\), and fiber volume fraction (Vf) was 40% in this case. The related theory of elasticity characteristic for in-plane random plate and for uni-directional plate was derived by Akasaka (1974). The simplified expression \(^6\) is as shown below.

\[
E_{\text{random}} = \frac{3}{8}E_L + \frac{5}{8}E_T
\]

The value of Young’s modulus \(E_L=16.6\) GPa(Vf:40%) of UD-Kenaf/PLA is proportionally converted as well as the Vf=21.8% of Washi-paper/PLA, and \(E_T\) was assumed as 3.92 GPa. Then, \(E_{\text{random}}\) was obtained as 6.42 GPa from equation (1). It was found that the value is almost the same level as \(E=6.20\) GPa of Washi-paper/PLA. This means that if the state of string can be obtained by the fiber of washi-paper and if it is molded with PLA, Young’s modulus equal to UD-Kenaf/PLA will be obtained.

4-5 Examination by the “rule of mixtures” of Young’s modulus

In composite materials, there is a relation of “rule of mixtures” concerning Young’s modulus like the following expression.

\[
E_{\text{compo}} = E_f \cdot V_f + E_m \cdot V_m
\]

That is, if the Young’s modulus of fiber \((E_f)\) and matrix \((E_m)\), and the volume content \((V_f)\) are known, Young’s modulus of the composite \((E_{\text{compo}})\) can be obtained. Therefore, Young’s modulus \((E_f)\) of Washi-paper is obtained from this equation conversely. As for the Washi itself, \(E_f=17.1\) GPa was obtained for Vf=21.8% of a three-layer composite.

5. Conclusions

From the aspect of a green composite, molding with Washi-paper and PLA was evaluated, and the basic tensile characteristics were found. Random strengthening Washi/PLA composite gave the experimental results for fiber volume fraction 21.8% as maximum strength 73.5 MPa, elongation 1.6%, and maximum Young’s modulus as 6.62 GPa. This means that if state of string can be obtained by the fiber of washi-paper and molded with PLA, a value equivalent to the Young’s modulus of UD-Kenaf/PLA will be obtained.

References
4) http://www.mitsui-chem.co.jp/info/lacea/