FABRICATION AND MECHANICAL PROPERTIES OF UNIDIRECTIONAL COMPOSITE OF SILK FIBER/PLA BY COMPRESSION MOLDING

A. Memon 1* and A. Nakai 2
1 Department of Advanced Fibro-Science, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto, 606-8585, JAPAN
2 Department of Mechanical Engineering, Gifu University, 1-1 Yanagido, Gifu, 501-1193, JAPAN
*E-mail: anin.memon@gmail.com

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1 General introduction

Natural fiber offer good opportunities as a reinforcement material for composites provides the positive benefit to the ecological and environmental advantage and the attractive mechanical properties. The explorations of natural fiber as green materials are alternative for synthetic polymer fiber in composite because of their advantages such as low cost, low density, renewability, biodegradability and acceptable specific strength. The natural fiber have been utilized for structural or semi-structural materials in various fields including aerospace, automotive, building, furniture, packaging and sport article [1-4]. Silk fibers are representative animal fiber of luster and fineness. They were spun out from silkworm cocoon produced by domesticated mulberry silkworm (Bombyx mori). Silk fiber consisted with fibrous protein termed fibroin that forms the thread core and glue-like protein termed sericin that surrounds the fibroin fibers to cement them together. Thus, long continuous fiber can only be spun when the sericin coating is removed from the cocoon structure. The process of sericin removal is usually called degumming, which is generally performed by soaking the silk fiber in boiling water, sometimes with salt or detergent to increase the efficiency of the process [5]. Silk fiber is a natural protein fiber which is biodegradable and highly crystalline with a well-aligned structure. It is well-known that it has higher tensile strength than glass fiber or synthetic organic fibers, good elasticity and excellent toughness. Silk fiber is also commercially available in a continuous fiber type [6-7].

Biodegradable polymers have recently been introduced in various fields as alternatives to traditional materials. Polylactic acid (PLA) is attracting attention as candidate of non petroleum based biodegradable polymer materials with high mechanical properties, thermal plasticity and biocompatibility. PLA is a highly versatile biopolymer derived from renewable resources like starch or sugar-base materials such as corn. It can maintain the mechanical properties in humid environment without suffered for rapid hydrolysis, therefore PLA can be a potential matrix in composite [6-9]. The combination of biodegradable polymer thermoplastics and renewable natural fiber such as silk as reinforcement in composite will answer the demand for environmentally friendly. Many researchers studied the processing technique for manufacturing silk fiber/PLA biodegradable composite [6-7, 9-12]. As referred to those literatures, biodegradable composites with silk fiber/PLA were manufactured with various processes by using silk fiber in short form. However, long form or continuous silk fiber in biodegradable composite has been rarely reported. In this study, the fabrication and mechanical properties of unidirectional continuous silk fibers reinforced biodegradable composites were investigated.

Many researchers have been studies the fabrication and mechanical properties of unidirectional
biodegradable composite. D. Plackett et al. [8] used PLA films with jute fiber mats to generate composites by a film stacking technique. The examination of composite fracture by scanning electron microscope showed voids in the composite. O. A. Khindker et al. [13] study processing technique for thermoplastic manufacturing of unidirectional composites reinforced with jute yarns. The intermediate materials called micro-braided yarn (MBY) were prepared by using braiding technique in which the jute spun yarn was straightly inserted as axial reinforcement fiber and polymer matrix fiber was braided around the reinforcing fiber. The composites were fabricated by compression molding. H. Katogi et al. [14] fabricated the unidirectional jute spun yarn reinforced PLA by using the jute fiber impregnated with resin. The prepregs were unidirectional laminated and hot pressed.

The objective of this study was to investigate the fabrication and mechanical properties of unidirectional silk fiber reinforced PLA composite. The parallel yarn configuration as shown in Figure 1 was used as intermediate materials to prepare the unidirectional composites by compression molding. Silk fiber from local product of Surin province, Thailand was shown in Figure 2. The unidirectional silk fibers reinforced PLA composite was characterized in the term of mechanical properties and the fabrication quality was examined by cross-section observation.

2 Materials and Experiments

The silk fibers having a fineness of ~23 tex were used as reinforcement fibers. The sericins of silk fibers were removed by soaking in boiling water. The continuous PLA fibers in a tow configuration were used as resin fiber, having a fineness of ~56 tex. Silk fibers were paralleled with PLA fibers and were used as intermediate materials (Figure 3). The preparation of parallel yarns was performed by using winding machine as shown in Figure 4. The fabrication of silk/PLA unidirectional composites involved twofold processes. The first step was performed by initially winding parallel yarn 20 times onto the metallic frame as shown in Figure 5. The metallic frame had a spring mechanism enabling it to adjust the tension caused by thermal shrinkage of fiber during processing. Before fabricate the specimens, the wound paralleled yarn were dried in convection oven at 80 °C for 2 hours. The molding dies for silk/PLA unidirectional composite fabrication are shown in Figure 6. The second step involved placement of the metallic frame containing the paralleled yarns in heated mold for consolidation to produce the specimens. The heated mold was cooled by water through the cooling system of the compression machine.

Consolidation process involved three stages. At first, under certain temperature, the solid fibrous matrix materials became softened and melt. In the second stage, under the heated mold and pressure, the matrix in the liquid form are soaked and infiltrated to the reinforcing fibers. The third stage is cooling, the matrix turned into solid form to hold the fiber in the definite position of unidirectional composite. Therefore the effects of molding temperature and impregnation quality were investigated. Thermo Gravimetric Analysis (TGA) was carried out on silk fiber and PLA by using analyzer (TA Instrument 2950) over the temperature range of 40-800°C with heating rate 50 °C/minute. The measurements were performed in the air atmosphere. According to the TGA data of silk fiber and PLA (Figure 7), the thermal resistance of the silk degrades at ~240 °C and PLA degrades at ~320 °C. Meanwhile the melting temperature of PLA was ~175 °C. Therefore, the processing window of molding temperature could be ~175-240 °C. In this study, the compression molding temperature was designed at 185, 195, 205, 215 and 225 °C. The compression molding was conducted with the pressure 1.33 MPa for 8 minutes.

The silk/PLA unidirectional composite specimens were fabricated with the dimension 200 x 20 millimeter. Thickness of specimens was ~1.0-1.5 millimeter. The middle parts of specimens were cut in the transverse direction with the length of 10 millimeter. They were applied in epoxy resin and then polished in order to observe the fiber impregnation by microscope. The tensile specimens with fiber axis along the loading direction were used in this study, they were clamped over the length of 50 millimeter at each end leaving a gauge length of 100 millimeter. Each end of tensile specimens was attached with the aluminum tab in the gripped area. Strain was measured using strain gauges which were bonded onto the central surface of specimens. The
tensile tests were conducted on an Instron Universal Testing Machine under the test speed of 1 millimeter/minute according to ASTM D638. In each molding condition, five unidirectional composite specimens were used for tensile test.

3 Results and discussion

The unidirectional composite specimens were fabricated (Figure 8). The thicknesses of specimens were changed and as a consequence the fiber volume fraction \( V_f \) was changed. Since the increasing of molding temperature led to decreasing the thickness of specimens, the volume fraction in composite specimens could be different as shown in Table 1. Thus, the achievement ratio of tensile modulus was used to compare the tensile properties among the specimens with different molding temperature [15]. The achievement ratio of tensile modulus was calculated by equation (1).

\[
\text{Achievement ratio of tensile modulus} = \frac{\text{Experimental modulus}}{\text{Theoretical modulus}} \quad (1)
\]

where, the experimental modulus was evaluated from tensile testing and the theoretical modulus value was calculated by rule of mixture.

The relationship between achievement ratio of elastic modulus and tensile strength, and molding temperature are shown in Figure 9. The achievement ratio of elastic modulus at molding temperature 195 \(^\circ\)C are similar to the molding temperature 205 \(^\circ\)C and increase when the molding temperature above 205 \(^\circ\)C. It is possible that the reduced viscosity of the resin at higher temperatures and hence better flow properties may have helped to improve resin impregnation and therefore led to trend of increasing achievement ratio of elastic modulus as the function of heating temperature. The achievement ratio of tensile strength of molding temperature 185 and 195 \(^\circ\)C are similar and decrease when the molding temperature was set above 195 \(^\circ\)C. Here, the effect of temperature on silk fiber was clarified. From the TGA measurement of silk fiber, the reduction rate of weight of silk fiber became more than 5% at temperature around 200 \(^\circ\)C. Therefore the achievement ratio of tensile strength was decreased due to heat deterioration of silk fiber while the molding temperature was increased. Silk fiber still remain the strength at molding temperature 185-195 \(^\circ\)C and decrease the strength at higher temperature.

The cross-section observation was performed to investigate the internal structure of unidirectional composite. Specimens with molding temperature of 185, 195 and 205 \(^\circ\)C showed good impregnation as shown in Figure 10, the fiber bundles were impregnated enough with PLA resin. According to the paralleled yarn of silk and PLA fibers, the architecture of this intermediate materials exhibits pore structure of macroscopic pores among fiber bundle and micro-pores of fiber inside bundle which lead to phenomena of macroscopic and microscopic impregnation in the unidirectional composite. Since the pressure was apply to the paralleled yarns in heated mold, the melt polymer first fill all space outside the yarns and then percolates towards the center of paralleled yarns. The rich regions of resin were seen between fiber bundle and good impregnation was found inside fiber bundle. Meanwhile, the crosses-section with molding temperature of 215 and 225 \(^\circ\)C showed poor impregnation because the viscosity of resin was decreased and the macroscopic flow occurred at higher temperature. Therefore thickness of composites was decreased, the volume fraction of composite was increased. The melt resins are flowed out from the molding die, good impregnation was found inside fiber bundle and less amount of resin among the fiber bundle.

From these results, the macroscopic flow of resin occurred while the molding temperature was increased, volume fraction was increased and the achievement ratio of elastic modulus was increased because of theoretical modulus was calculated in considering the real volume fraction. While increasing the molding temperature, the achievement ratio of tensile strength was decreased because of silk fibers were deterioration and the melt resins were flowed out from unidirectional composite due to the macroscopic flow of low viscosity resin. Therefore the optimum compression molding temperature was 185 - 195 \(^\circ\)C for fabrication of unidirectional silk fiber reinforced PLA composite.
4 Conclusions

The silk/PLA unidirectional composites were fabricated and effect of the molding temperature on the mechanical properties and impregnation quality were investigated. It was clear that the volume fraction of composite were increased with increasing the molding temperature due to the macroscopic flow of low viscosity resin and the achievement ratio of elastic modulus was increased because of theoretical modulus was calculated in considering the real volume fraction. While increasing the molding temperature, the achievement ratio of tensile strength was decreased because of deterioration of silk fiber. The investigation on fabrication and mechanical properties of silk/PLA unidirectional composites is to be applied to guide the manufacturing process concerning selection of appropriate raw materials and optimized processing conditions of unidirectional bio-composite products by compression molding.

References


Fig. 1. Schematic of parallel yarn

Fig. 2. Silk fiber from local product of Surin province, Thailand
Fig. 3. The intermediate materials silk/PLA fiber

Fig. 4. The parallel technique by using winding machine

Fig. 5. Schematic of consolidation set up for silk/PLA unidirectional composite
Fig. 6. Molding die for silk/PLA unidirectional composite fabrication

![Molding die images]

a) Upper die  
b) Metallic frame  
c) Lower die

![TGA data graph]

Fig. 7. TGA data of silk fiber and PLA

Table 1: Thickness and fiber volume fraction

<table>
<thead>
<tr>
<th>Specimens No.</th>
<th>Molding temp. (°C)</th>
<th>Thickness (mm)</th>
<th>$V_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>185</td>
<td>1.53</td>
<td>37.4</td>
</tr>
<tr>
<td>2</td>
<td>195</td>
<td>1.48</td>
<td>40.3</td>
</tr>
<tr>
<td>3</td>
<td>205</td>
<td>1.36</td>
<td>43.1</td>
</tr>
<tr>
<td>4</td>
<td>215</td>
<td>1.13</td>
<td>46.2</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>1.02</td>
<td>48.0</td>
</tr>
</tbody>
</table>
Fig. 8. Fabricated unidirectional composite specimens

Fig. 9. Relationship between achievement ratio of tensile modulus and strength and molding temperature
Fig. 10. The cross-section observation of silk/PLA unidirection composite with varying the molding temperature