

Manufacture of Continuous Glass Fiber/Polylactic Acid (PLA) Composite and Its Properties

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Abstract

The continuous glass fiber reinforced polylactic acid (PLA) prepreg was manufactured by direct melt impregnation. The mechanical and thermal properties of PLA prepreg were observed. The properties of PLA prepreg were compared with the neat PLA and the injection molded glass fiber/PLA composite. The PLA prepreg having a fiber volume fraction of 27.7 % shows well enhanced tensile strength of 331.1 MPa, flexural strength of 528.6 MPa, and flexural modulus of 24.0 GPa. The enhancement in the heat deflection temperature (HDT) and the crystallinity were also observed. The fracture interface was inspected by FE-SEM. The degree of impregnation as a function of pulling speed was measured. The degree of impregnation at the pulling speed of 5 m/min reached over 90 % in this research.

Keywords: Continuous glass fiber; prepreg; fiber reinforced thermoplastic; heat deflection temperature (HDT); mechanical properties; polylactic acid (PLA)

1. Introduction

Polylactic acid (PLA) is one of bio-degradable polymers being used widely from as packaging material to medical applications [1, 2]. In these days, applications to automobiles have attracted industrial attention. However, eco-friendly materials, in many cases, have weak thermal stability to be used for vehicles. PLA, on the other hand, has better performance than other bio-degradable polymers. Nevertheless, it has disadvantages of low crystallinity and low heat deflection temperature (HDT). For example, the HDT of PLA (NatureWorks LLC, 4032D) is 50.4 °C while the HDT of polypropylene (PP) is 108 °C [3, 4]. PP is one of the most widely used polymers for automotive applications and the HDT of PLA is much lower than the value required for automotive industry. In order to increase the HDT of a polymer, there are several ways such as increasing the glass transition temperature, T_g, applying reinforcement, and increasing the crystallinity. Generally, higher aspect ratio of reinforcement in the matrix gives better reinforcing effect. Furthermore, it is well known that the crystallinity can be increased at high shear rates [5]. Therefore, in this study, continuous glass fiber was chosen for the reinforcement and the melted PLA resin was impregnated into the continuous fiber tow by using the direct melt impregnation

method to induce high shear rates. The direct melt impregnation method is common technique and there are several variations in the process by combining elements such as fixed pin, porous impregnation wheel and freely rotating pin [6]. In this study, the melt pool with fixed pins was applied to impregnate PLA resin into the continuous fiber tow.

Higher shear rate can be applied to the PLA resin by forcing the resin to flow between the continuous fibers. This can be achieved by inducing resin pressure through pulling the fiber tow over the impregnation pin. For the PLA prepreg thus manufactured, degree of impregnation as a function of pulling speed was observed as well as mechanical properties, crystallinity, HDT, and the fracture surface.

2. Experiment

2.1. Materials

PLA resin (NatureWorks LLC, 4032D) was used for the matrix of prepreg. The glass fiber (Owens Corning, 2400 tex) was used for the reinforcement. The fiber diameter was 22.4 μm and the width of the fiber bundle was 6 mm. The roving was treated with the same sizing for PP matrix.

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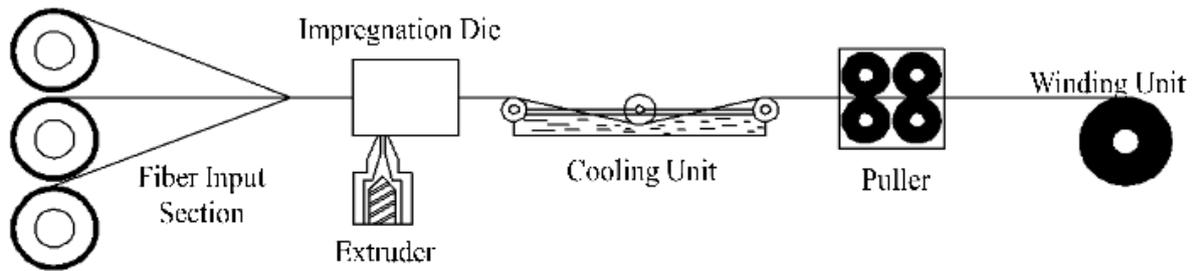


Figure 1. Illustration of the setup for manufacturing PLA prepreg.

Table 1. Thermal properties of neat PLA and PLA prepreg

| | T_g (°C) | T_c (°C) | T_m (°C) | ΔH_m (J/g) | X_c (%) |
|-------------|------------|------------|------------|--------------------|-----------|
| Neat PLA | 59.03 | 105 | 166 | 17.1 | 18.2 |
| PLA prepreg | 58.2 | 110.9 | 165.2 | 16.85 | 32.4 |

2.2. Setup for manufacturing of PLA prepreg

The setup consisted of 5 components: unwinding unit, pin impregnation die, cooling unit, puller and winding unit. Fiber bundle was unwound with a constant tension by using the unwinding unit. The constant tension is important to control the input position of fiber bundle [7, 8]. The guided fiber bundle was impregnated by using the direct impregnation method. The pin impregnation die consisted of three 10 mm diameter cylindrical pins and two 8 mm diameter cylindrical pins. At the bottom and upper plate of the pin impregnation die, the heaters were introduced to maintain the preset temperature for the resin at 220°C. The consumed resin was replenished by the extruder continuously. A single screw extruder (Uenoyama Kiko) was used to deliver the molten resin into the pin impregnation die. The impregnated fiber bundle after the pin impregnation die was cooled by using a water cooling vat. The caterpillar type puller was applied to pull the fiber bundle. The pulling speed was controlled from 0.5 m/min to 5 m/min. After the puller, the prepreg was wound with a constant torque by the winding unit. The illustration of the setup for manufacturing of the PLA prepreg is shown in Fig. 1.

2.3. Characterization

The tensile strength, the flexural modulus and strength, and the inter-laminar shear strength of the manufactured specimens were measured using a universal testing machine (UTM) (Lloyd Instruments, LR 50K). In order to obtain a data point, at least five tests were done and the results were averaged.

The tensile strength was measured following ASTM D 3039/D 3039M standard with the crosshead speed of 2 mm/min. The flexural strength and modulus were measured according to ASTM D 790 with the crosshead speed of 5 mm/min. Testing of the inter-laminar shear strength of the specimens was done following the ASTM D 5379/D 5379M with the crosshead speed of 2 mm/min.

The fiber volume fraction of PLA prepreg was observed by a close inspection of polished cross-sections

of impregnated samples with five test values per one condition. A microscope (Leica, Type 020-520.008 DM/LM) with a mounted CCD camera (Nikon, Coolpix 950) was used to observe the polished cross-section of the prepreg. The test specimens were mounted with epoxy resin and the cross-sections were polished using a series of sand papers with increasing finish (400, 800, 1200, 2400 and 4000 grains/in).

The crystallization behavior was observed by differential scanning calorimetry (DSC) (Perkin Elmer, DSC7) in N₂ atmosphere. In the DSC analysis, the samples were first heated to 200 °C with the temperature increasing at a rate of 10 °C/min. After complete melting, the samples were cooled down to 30 °C at a rate of 10 °C/min. They were then heated again to 200 °C at a rate of 10 °C per a minute. In this way, the crystallization as well as the melting curves of the composite was obtained. The crystallinity of PLA prepreg could be evaluated using the following equation:

$$X_c = \frac{\Delta H_m}{W_p \Delta H_m^0} \quad (1)$$

where W_p is the weight fraction of the polymer, ΔH_m the measured melting enthalpy, and ΔH_m^0 the melting enthalpy of the 100% crystalline PLA. ΔH_m^0 is taken as 93.7 kJ/kg from the literature [9].

The heat deflection temperature (HDT) was measured following ASTM D648 using the heat distortion tester (Toyoseiki, M-2). For the test, a constant load of 0.46 MPa was applied at the center of the three-point bending flexural coupon bar sample. The sample was heated from the room temperature to 200 °C at a rate of 2 °C/min.

The specimens used for the tests were made from the prepreg prepared using the manufacturing setup mentioned above. For producing the prepreg continuously, the pulling speed of 1 m/min and the setting temperature of 220 °C were applied.

3. Results and Discussion

3.1. Degree of impregnation

The degree of impregnation as a function of pulling speed was observed by using the microphotographs of the cross-sections of samples. It was defined as the ratio between the number of impregnated fibers and the total number of fibers in a tow. The results are shown in Fig.2. From the 1 m/min to the 5 m/min of pulling speed, the degree of impregnation was over 90 %. Especially, the degree of impregnation at the pulling speed of 5 m/min reached 92.5 %.

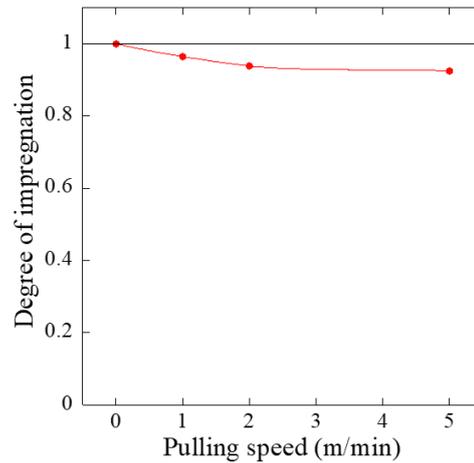


Figure 2. Degree of impregnation as a function of pulling speed

3.2. Mechanical properties

The incorporation of continuous glass fibers into PLA matrix produces an enhanced tensile and flexural strengths and a higher flexural modulus in the fiber axis direction. The average tensile strength of PLA prepreg was 331.1 MPa, the average flexural strength of PLA prepreg was 528.6 MPa, and the average flexural modulus of PLA prepreg was 24.0 GPa. Compared with the neat PLA and the injection molded glass fiber/PLA composite having a fiber volume fraction (Vf) of 17.0 %, the PLA prepreg having a fiber volume fraction (Vf) of 27.7 % shows much higher strength than the neat PLA (tensile strength: 62.9 MPa, flexural strength: 98.8 MPa) and the injection molded glass fiber / PLA composite (tensile strength: 80.2 MPa, flexural strength: 108.9 MPa) [10].

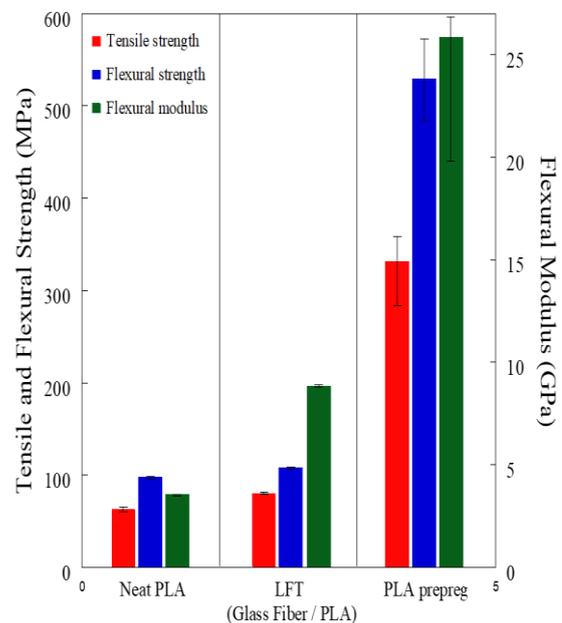


Figure 3. Mechanical properties of the composite specimen made with PLA prepreg

The flexural modulus was about 7.3 times larger than that of the neat PLA (flexural modulus: 3.3 GPa), about 2.9 times larger than the injection molded glass fiber/PLA composite (flexural modulus: 8.2 GPa). The average inter-laminar shear strength of PLA prepreg composite in the perpendicular direction of fiber axis was 33.2 MPa. The results are shown in Fig. 3.

3.3. Crystallization

The glass transition temperature (Tg), the crystallization temperature (Tc), and the melting temperature (Tm) of the PLA prepreg composite were observed by the DSC. The results are shown in Table 1.

As can be seen, Tg and Tm of the PLA prepreg were not changed notably from the neat PLA, while Tc and the crystallinity were increased. Crystallinity of the PLA prepreg was increased to 32.4 % from 18.25 % of the neat PLA. The increase in the crystallinity is likely due to the high shear rate applied during impregnation. The application of shear is known to increase the orientation of the molecular chain in the polymer melt and the nucleation rate [5] and thus to facilitate crystallization. Ultimately, the increase in the crystallinity of PLA prepreg is believed to affect the increase of mechanical properties.

Table 2. HDT of neat PLA and PLA prepreg

| | HDT (°C) |
|--------------|----------|
| Neat PLA [3] | 50.4 |
| PLA prepreg | 100 |

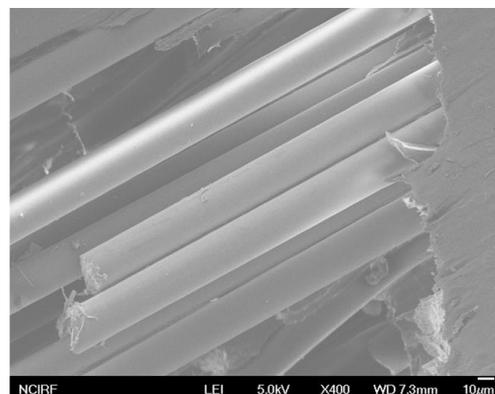


Figure 4. Fracture interface of tensile test specimen made with PLA prepreg

3.4. Heat deflection temperature (HDT)

The HDT of PLA prepreg composite was enhanced as shown in Table 2. The HDT of PLA prepreg composite was 100 °C while the HDT of neat PLA was 50.4 °C. There are several reasons for the increase in the HDT of polymer; increase of T_g, presence of the reinforcement, and increase in the crystallinity. Above all, the introduction of high aspect ratio reinforcement and the increase in crystallinity were considered as main reasons for the increase in HDT in this study.

3.5. The fracture interface

The fracture interface of tensile test specimen of PLA prepreg composite was observed with FE-SEM (JSM-6700F, JEOL) as shown in Fig.4. As can be seen, surface of glass fibers was clean and the PLA was not elongated well. It shows that the adhesion between the PLA and glass fiber is weak.

4. Conclusions

The manufacture and evaluation of PLA prepreg were considered. At the pulling speed of 5 m/min, the degree of impregnation was over 90 %. For the PLA prepreg, the mechanical properties were considerably increased. Besides the high aspect ratio of reinforcement, the high shear rate during the processing and the resulting crystallinity were thought to be responsible for the increase in mechanical properties and thermal stability. For the manufacturing of PLA prepreg, the direct melt impregnation method seemed to be working and served the purpose. The necessity of modification of the interface between the fiber and the matrix was evident.

Acknowledgement

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