Boosting the Performance of CFRP with High Axial Compression Characteristics Fabricated Using the Filament Cover Method: Surface Modification of Sheath Filament PBO Fiber and Improvement of Reinforcing Fiber Volume Fraction

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Abstract

We have proposed the filament cover method for fabricating carbon fiber-reinforced plastic (CFRP) with high axial compression characteristics to address one of the shortcomings of unidirectional CFRP, whose compressive strength is inferior to its tensile strength. In this paper, we attempt to fabricate CFRP with high compressive strength while retaining the high tensile strength of unidirectional CFRP. We propose a method for surface modification of sheath filament PBO fiber (corona discharge treatment followed by silane coupling treatment) and a method for increasing the reinforcing fiber volume fraction of CFRP (flattening reinforcing fiber bundles and shrinking the gaps between them). CFRP prototypes fabricated using them exhibit tensile strength on par with regular CFRP, the effectiveness of the method was confirmed.

Key Words: CFRP, Axial compression characteristics, Filament cover method, Surface modification, Fiber volume fraction

1. Introduction

Due to its excellent mechanical properties, fiber reinforced plastic (FRP) is used in a variety of fields and applications, including aerospace, automobiles, and sporting equipment. FRP is resistant to tension but susceptible to compression along the fiber axis, and reports in the literature indicate an inability to take full advantage of the material’s excellent mechanical properties [1]. For example, unidirectionally fiber reinforced CFRP and GFRP have a compressive strength to tensile strength ratio of 0.71 [2] and 0.49 [3], respectively. Most mechanical structures are used under conditions of bending and compression. Application of an axial load to FRP causes the thin reinforcing fibers to bend, leading to buckling and the formation of a kinking band. As a result, the FRP fails at a level of stress that is much lower than its tensile strength would suggest. Application of a bending load to a mechanical structure’s FRP shell imposes tension on one side of the structure and compression on the other. There is demand from manufacturers for simple, effective methods for increasing the compressive strength of unidirectionally fiber reinforced FRP.

The filament cover method, illustrated in Fig. 1, has been proposed in the literature [4]. By winding 166 small bundles of high-strength PBO filament (HM, Toyobo Co., Ltd.) around...
bundles of reinforcing carbon fiber (T300B-3K, Toray Co., Ltd.) and banding the reinforcing fibers at a short interval to increase buckling load of the fiber bundles, it has been confirmed that compressive strength can be significantly improved such that the ratio of the CFRP’s compressive strength to its tensile strength in the axial direction improves to a value of 1 or greater. However, CFRP whose axial compression characteristics have been improved by means of the filament cover method suffers from a shortcoming: its sheath PBO fibers, whose surfaces are untreated, adheres poorly to epoxy resin. Reduced reinforcing fiber volume fraction likely prevents the material from exhibiting the high tensile characteristics that are otherwise associated with CFRP.

In this paper, we propose a method for modifying the surface of the PBO fibers to facilitate improved adhesion to epoxy resin so that the resulting CFRP exhibits not only high compressive strength, but also tensile strength on par with regular CFRP. We also propose a method for increasing the reinforcing fiber volume fraction of CFRP fabricated using the filament cover method and verify its efficacy.

2. Surface modification of PBO fibers and evaluation of adhesion with epoxy resin

PBO fiber is an organic fiber, recently are widely used in composite materials because of their highly specific tensile strength, modulus, and thermal resistance [5]. A new high performance PBO fiber is the rigid-rod crystal polymer, i.e., it is the polybenzazole containing aromatic hetero-cyclic ring [6]. Especially, PBO fiber is known to have poor interfacial adhesion due to the lack of polar functional groups in their repeat units. In order to apply the PBO fiber as a reinforcing material, surface modification is needed to enhance their stress transferring effect [7].

Young et al. studied the distribution of interfacial shear strength (IFSS) along embedded fibers for corona [8] and thermal [9] treated PBO fiber/epoxy composites. They demonstrated that corona treatment was more effective at improving IFSS than thermal treatment. For both corona and thermal treatment, interfacial adhesion increased due to the improvement of the PBO fiber’s surface roughness. However, the IFSS between the fiber and matrix was not significantly changed.

Hailin is typical of the many papers describing surface modification of PBO fibers via direct reaction with a coupling agent or other chemical reagent [10]. However, the approach yields only limited effects due to the stable molecular structure of the fibers’ surface, which makes it difficult for chemical bonds to form.

To improve adhesion between PBO fibers and resin, we attempted a fiber surface treatment method that combines corona treatment, which promotes physical bonds by increasing surface roughness, with coupling agent treatment, which adds a functional group that bonds readily with resin to the fibers’ surface.

2.1 Surface modification of PBO fibers

Using a corona surface modification device (PS-1M, Shinko Electric Co., Ltd.), we applied the discharge electrode to the fiber at a power of 10 kV and a speed of 0.5 m/s and repeated the treatment 10 times.

For the coupling agent treatment, we performed the procedure illustrated in Fig. 2 using KBM-403 (3-glycidoxypropyl triethoxysilane, Shin-Etsu Chemical Co., Ltd.), which combines an epoxy group with a reactive functional group. The surface treatment liquid was mixed with a silane coupling agent and water (weight ratio 100: 2). PBO fiber were immersed in the treatment liquid, and the surface is modified while vibrating for 1 hour using an ultrasonic vibrator. After that, the PBO fibers are dried using a vacuum dryer.

![Surface modification with a coupling agent.](image)

Table 1 describes the combination of fiber surface modifications. P1 indicates the PBO fiber in its original state, with no surface modification applied, P2 and P3 respectively subjected to corona fiber/epoxy treatment, while P4 indicates corona surface modification followed by coupling agent treatment. P5 indicates coupling agent treatment followed by corona surface modification.

| Surface modification combinations. |
|-----------------------------------|
| **P1** | None |
| **P2** | Corona only |
| **P3** | Coupling only |
| **P4** | Corona + coupling (Corona surface modification followed by coupling agent treatment) |
| **P5** | Coupling + corona (Coupling agent treatment followed by corona surface modification) |

T300B-3000 carbon fiber (Toray Co, Ltd.) was used to fabricate the reinforcing fiber bundles. Reflecting the need for a material
with a high Young’s modulus in order to hold the reinforcing fiber bundles in place and a small number of fiber strands so that the reinforcing material’s fiber content percentage would not decrease. Zylon HM PBO fiber (Toyobo Co., Ltd.) was used for the cover filaments. At 66, the material has a low fiber count. Table 2 provides details, based on values from the manufacturer’s catalog. Epoxy resin (Denatite XNR 6815, Nagase Chemtex Corporation) and curing agent (Denatite XNH 6815, Nagase Chemtex Corporation) were used as the matrix.

Table 2 Physical properties of fibers.

| Fiber name | Carbon fiber | PBO fiber |
|------------|--------------|-----------|
| Fiber type | T200B-3000   | Zylon HM  |
| Decitex (dtex) | 1980 | 273       |
| Filaments (pieces) | 3000 | 66        |
| Density (g/cm³) | 1.76 | 1.56      |
| Tensile strength (GPa) | 3.53 | 5.8       |
| Tensile modulus (GPa) | 230 | 270       |

2.2 Evaluation of adhesion between PBO fibers and epoxy resin

In order to assess how well resin adheres to PBO fibers, it is necessary to measure the IFSS. The fragmentation test method [11], which is often used in IFSS measurement, is poorly suited to measuring the IFSS of PBO fiber due to the material’s high fracture elongation. Meanwhile, the micro-droplet method [12], which is used by commercial measurement machines, yields results with high variability due to the softness of PBO fiber. Referring to the pinhole-type single-fiber pull-out test proposed as a method for IFSS measurement by Kanai et al. [13], we made modifications to enable IFSS measurement of PBO fiber without requiring a dedicated machine.

Fig. 3 provides an overview of the manner in which samples were fabricated and IFSS measurement performed. In Fig. 3(a), uncured epoxy resin is injected into the pinhole in a pinhole plate, which consists of an aluminum plate (thickness: 0.5 mm) with a hole (diameter: 0.3 mm) in its center. Then a single fiber is inserted into the pinhole, and the resin is cured to create a pinhole test specimen (Fig. 3(B)). The depth of fiber insertion is adjusted while viewing the process with a digital microscope. Then, as shown in Fig. 3(c), an aluminum plate that is connected to a tensile tester’s load cell is adhered to the top part of the fiber using instant glue while adjusting the x-y stage. The tensile test is then carried out at a speed of 0.05 mm/min. using an Auto Graph (AG20kN, Shimadzu Corporation) and load cell (SBL-1N, Shimadzu Corporation).

Fig. 4 illustrates an example measurement (carbon fiber and epoxy resin). Using an SEM, the length of the embedded portion of the fiber and the diameter of the fiber (as averaged at 5 locations) are measured (Fig. 4(b)). Then the IFSS is calculated based on...
the maximum pull-out load (From Fig. 4(a) Pull-out load vs. displacement curve). in the pinhole-type single-fiber pull-out test. IFSS values for the measured carbon fibers were roughly the same as the results of the fragmentation test [11], demonstrating the validity of the method.

2.3 IFSS measurement results

![IFSS measurement results for fibers with and without surface modification](image)

Fig. 5 IFSS measurement results for fibers with and without surface modification.

Fig. 5 summarizes IFSS measurement results for each of the fiber surface modification conditions. When fabricating CFRP using carbon fiber and epoxy resin, manufacturers subject fibers to surface modification. The resulting adhesion conditions, which are typical, are considered within the FRP industry to satisfy the CFRP’s mechanical characteristics. The figure includes the carbon fiber/epoxy IFSS value for comparison purposes. As can be seen, untreated PBO fiber/epoxy has a low IFSS value that is less than 30% that of carbon fiber/epoxy. The adhesion between the fiber and resin is likely too low for application in FRP. Corona and coupling modification yielded improvements of 80% and 140% in IFSS values, respectively. Sample P4 had the highest value for PBO fiber, with an improvement of 220%, and reached 85% of the IFSS value of carbon fiber/epoxy. This result indicates the effectiveness of the surface modification method (P4) combining corona modification, which increases fibers’ surface roughness to promote physical bonding, and coupling modification, which adds a functional group that bonds readily with resin to the fiber surface.

3. Improvement of the reinforcing fiber volume fraction

The reinforcing fiber volume fraction of FRP significantly affects the material’s strength and elastic modulus. Use of the filament cover method raises concerns about lowering the reinforcing fiber volume fraction of the fabricated FRP.

Fig. 6(a) illustrates a unidirectional fiber reinforced sheet made from normal carbon fiber. Fig. 6(b) illustrates a sheet with filament-covered fiber bundles fabricated using the conventional method for producing unidirectionally fiber reinforced sheets, which results in a larger interval between fiber bundles and a lower reinforcing fiber volume fraction. In Fig. 6(c), the interval between fiber bundles has been reduced as much as possible.

CFRP with high axial compression characteristics fabricated using the filament cover method has a lower carbon fiber volume fraction due to the use of the covering filament, as illustrated in Fig. 6(c). Covering filament usually consists of bundles of 1000 PBO fibers, but in a previous paper [4] we described how the separation method allows use of bundles of 166 PBO fibers. In this study, we used an even smaller number of PBO fibers per bundle (66, supplied by Toyobo Co., Ltd.).

Carbon reinforcing fiber sheets used in CFRP use flattened fiber bundles to increase the fiber volume fraction, as shown in Fig. 6(a). However, carbon fiber bundles fabricated using the filament cover method are round, as shown in Fig. 6(c). The area shown in red frame becomes resin-rich, and the FRP’s reinforcing fiber volume fraction decreases.

![Unidirectional reinforced fiber sheet and reinforced fiber volume fraction](image)

Fig. 6 Unidirectional reinforced fiber sheet and reinforced fiber volume fraction.

![Flattening of fiber bundles by a press](image)

Fig. 7 Flattening of fiber bundles by a press.
We attempted to flatten fiber bundles through the application of pressure. As shown in Fig. 7, we prepared a sheet of filament-covered carbon fiber bundles, placed it in a mold (thickness: 0.3 mm), and compressed it in a press to flatten the fibers. However, the bundles returned to their original shape over time once removed from the mold. As a result, we attempted a method to retain the flattened shape, as described below.

We inserted a nylon monofilament (diameter: 0.1 mm) when covering the carbon fiber bundles (Fig. 8). We then inserted a sheet of the filament-covered carbon fiber bundles in the mold and compressed it while heating it in a hot press to flatten the bundles (Temperature: 253 °C, pressure: 3MPa, heating time: 30 minutes). We cooled the sheet while it was still under pressure so that the flattened shape would be retained.

Fig. 9 illustrates the results of measuring the change in thickness over time after cooling. Each result was obtained by averaging measurements for 5 sample. The sheets were 0.3 mm thick when they were removed from the mold, but the sheet of regular filament-covered carbon fiber bundles returned to a thickness of greater than 0.35 mm over time. The sheet of filament-covered carbon fiber bundles incorporating the nylon monofilament maintained a thickness of roughly 0.3 mm, indicating that the flattened shape was retained.

4. Tensile characteristics of CFRP fabricated using the filament cover method

To verify the efficacy of the methods proposed here, we investigated the tensile characteristics of CFRP fabricated using the methods described in sections 2 and 3 above.

Using the optimal conditions (P4) identified in section 2, we subjected sheath PBO fibers to surface modification. When then used those PBO fibers to fabricate filament-covered reinforcing fiber bundles using the filament cover method. We also fabricated a unidirectionally reinforced fiber sheet using the method for improving the reinforcing fiber volume fraction described in section 3. We then layered the two together and fabricated CFRP sheet samples using the VARTP method [4]. Table 3 lists the sample types and associated reinforcing fiber volume fractions.

| Types of CFRP                        | Reinforcing fiber volume fraction (%) |
|--------------------------------------|--------------------------------------|
| CFRP (no treatment)                  | 53.4                                 |
| CFRP + cover                         | 30.6                                 |
| CFRP + cover + high density          | 50.7                                 |
| CFRP + cover + high density +        | 51.0                                 |
| surface modification                  |                                      |

For comparison purposes, we fabricated a regular unidirectionally reinforced CFRP sheet, labeled “CFRP (no treatment).” The “CFRP + cover” samples consisted of CFRP produced using the filament cover method as described previously. The “CFRP + cover + high density” samples were fabricated using the method described above for increasing the reinforcing fiber volume fraction. The “CFRP + cover + high density + surface modification” samples added surface modification of the PBO fibers to the above. As indicated in Table 3, the method described in section 3 increased the reinforcing fiber volume fraction to a level approaching that of the “CFRP (no treatment)” samples. Increasing the CFRP reinforcing fiber volume fraction shrinks gaps between fibers and thereby interferes with bending and buckling of the fibers. The compressive strength of the CFRP likely improves as a result of the mechanism of compression failure in the CFRP fiber axial direction as described in papers [2] and [4].

Tensile testing was performed in accordance with JIS K7073 in order to evaluate the mechanical characteristics of the CFRP samples. Samples measured 140 mm (L) by 15 mm (W) by 2 mm (thickness), and the tab length was 30 mm. An Auto Graph AG-20KND (Shimadzu Corporation) was used to perform the test. The sample speed $V$ was 1.0 mm/min, and 5 or more samples of each type were prepared.
We proposed methods for modifying the surface of PBO fiber and increasing the CFRP reinforcing fiber volume fraction in CFRP with high axial compression characteristics fabricated using the filament cover method in order to give the material high compressive strength while retaining the high tensile strength of CFRP. We then fabricated CFRP using those methods.

We found that a surface modification method consisting of corona discharge treatment and silane coupling treatment is an effective way to improve adhesion between PBO fiber and epoxy resin. We also found that the proposed methods shrink the gaps between reinforcing fiber bundles and flatten those bundles, improving the CFRP reinforcing fiber volume fraction.

The results demonstrate the efficacy of the proposed methods.

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