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Carbon-fiber-reinforced polypropylenes often exhibit insufficient mechanical properties because of low affinity between the carbon fibers (CFs) and the matrix resins. From the viewpoint of designing materials with better properties, it is important to control the interfacial properties. In this study, the interfacial properties are quantified in terms of the interfacial shear strength (IFSS), and the relationships among the IFSS, composite strength, and impact resistance are evaluated. When the fiber length is sufficiently short (as in injection-molded materials), the composite strength and impact resistance improve with increasing IFSS. On the other hand, when the fiber length is longer, the impact resistance improves with decreasing IFSS. Longer CFs with low IFSS require higher energy to pull out from the matrix resin than that required for interfacial debonding.

Keywords: CFRP; thermoplastics; interfacial shear strength; impact strength; fiber length

1. Introduction

In recent times, carbon-fiber-reinforced plastics (CFRPs) have been extensively applied in various industries owing to their excellent mechanical properties and low weight. These characteristics make them particularly suitable for applications in the transportation industry because of the strong need therein for fuel efficiency and reduced environmental load.[1,2] For some years, CFRPs have been aggressively adopted in the aerospace industry; more recently, the automotive industry has also investigated the use of CFRPs, especially for application to electric vehicles.

The adoption of CFRPs in production vehicles requires a high-cycle process and recycling technology. Already, some automotive parts are being made of CFRPs with thermosetting resin.[3] Such parts are usually molded using methods such as prepreg/autoclave, resin transfer molding, and filament winding. CFRPs are clearly excellent solutions for reducing the weight of vehicles; however, thus far, their application has been limited to luxury vehicles and high-end sports cars owing to productivity issues. In this light, CFRPs with thermoplastic resin, the use of which enables a high-cycle process, have recently been widely investigated. In particular, polypropylene (PP) has attracted attention as a matrix resin because it is lightweight, waterproof, and inexpensive.

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The weight of a vehicle can be effectively reduced by applying CFRPs to large parts such as door modules, hoods, and roofs. Such parts are commonly manufactured using press molding. However, conventional FRP sheets such as glass-mat-reinforced thermoplastics that are used in press molding are not widely applied to such parts because their weight reduction effect is limited. The molded products also suffer from problems related to the fiber orientation and heterogeneity.

Additionally, PP is known to show poor adhesion to carbon fibers (CFs).[4] CFRPs with homo or block PP show poor mechanical properties. On the other hand, CFRPs with acid-modified PP show improved interfacial strength; the increased adhesion is attributed to interaction between functional groups on the CF surface and the acid-modified PP.[5] To evaluate the interfacial adhesion, the single-fiber composite (SFC) method was developed for thermoplastic resin.[6] The SFC method can be used to quantitatively discuss the interfacial shear strength (IFSS) and mechanical properties of CFRPs.

Recently, Toray Industries developed a new isotropic CFRP sheet using discontinuous CFs (Figure 1). Owing to the controlled fiber length and individual fiber dispersion, this sheet shows excellent weight reduction effect that is nearly equal to that of a continuous fiber-used prepreg.[6,7] A magnified photograph of the CFRP sheet is shown in the right-hand side of Figure 1; CFs are observed to be dispersed individually and homogeneously.

This study investigates the effects of the fiber length and IFSS on the mechanical properties of CFRPs.

2. Experimental

2.1. Materials

Seven-millimeter-long chopped CFs (Toray Industries, Inc.; T700S; tensile modulus: 230 GPa; tensile strength: 4900 MPa) were used. A CF mat (Toray Industries, Inc.; surface area: $300 \times 300\ mm^2$; weight per area: $100\ g/m^2$) was also used.[8]

PP was obtained by melt-mixing homo PP (Mitsui Chemicals Ltd.; melt flow rate (MFR): 15 g/10 min @230 °C) and acid-modified PP (Mitsui Chemicals Ltd.; QF500; MFR: 3 g/10 min @230 °C) by using a twin-screw extruder TEX30α (screw diameter $D = 30$ mm; $L/D = 31.5$, where L is the screw length; screw speed: 150 rpm; production speed: 8 kg/h). The barrel temperature was 210 °C. The extruded strand was cooled in a water bath and pelletized. The pellet was dried in vacuum at 50 °C for more than 3 h.

PP film was obtained by melt-pressing. An amount of 20 g of the obtained pellet was set between the releasing sheets (Teflon®; thickness: 1 mm). This pellet was set on

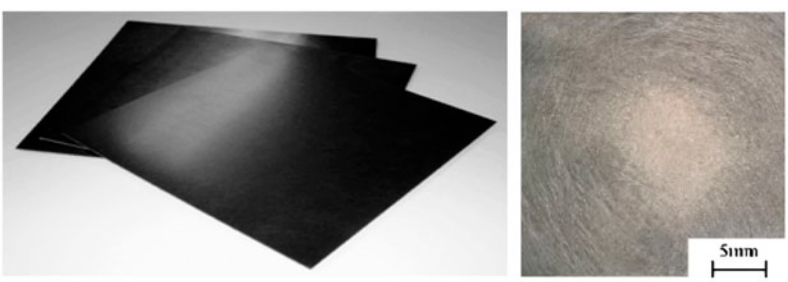


Figure 1. Unidirectional carbon-fiber-reinforced thermoplastic sheet.

a 37-t hydraulic press machine and heated at 200 °C for 2 min under 0.8 MPa pressure. The melted film was cooled at 30 °C for 1 min under the same pressure. After removing the releasing sheets, a $300 \times 300\,mm^2$ section of the obtained PP film was cut out. The film thickness was 220 μm ($200\,g/m^2$).

An injection-molded test piece was manufactured using a microcompounder (DSM Xplore; Compounder 15; screw length: 135 mm; barrel volume: 16.5 mL) and an injection molder (DSM Xplore; mold temperature: 40 °C). The PP pellet was melt-mixed at 60 rpm for 2 min. The barrel temperature was 200 °C. The extruded strand was directly injected-molded, and test pieces were obtained.

A CFRP sheet was obtained by melt-pressing CF mats and PP films. Six CF mats (surface area: $300 \times 300\,mm^2$) and PP films were laid up against each other and placed between releasing sheets (Teflon®; thickness: 1 mm). This laminate was set on a 70–t hydraulic press machine and heated at 220 °C for 2 min under 4 MPa pressure. The resin sheet was cooled under the same pressure until the material temperature reached 50 °C, and a 1.6 mm thick CFRP sheet was obtained. Then, the two obtained sheets were laid up against each other and set on a 70-t hydraulic press machine as before. The laminate was heated under 2 MPa pressure until its center reached a temperature of 210 °C. The sheet was cooled under 5 MPa pressure until its temperature reached 50 °C, and a 3.1 mm thick CFRP sheet was obtained.

2.2. Test methods

A three-point flexural test was conducted according to ASTM D790 (crosshead speed: 1.4 mm/min; specimen width: 25 mm; length: 50 mm; and thickness: 1.6 mm). The Izod impact test was conducted according to ASTM D256 Method A. A notched test piece was impacted in the edgewise direction.

The average fiber length (L_{av}) of the CFRP sheet is calculated as follows. The matrix resin was removed from the CFRP sheet by heating at 500 °C for 1 h using an electric furnace (Koito Industries, Inc.; KPD-31 N). Four hundred CF filaments were picked up, and the length of each fiber (L_i) was measured using a digital microscope (Keyence Corporation; VHX-500). L_{av} was calculated as

$$L_{av} = \frac{\sum L_i}{400} \quad (1)$$

The interfacial strength between CF and PP was evaluated by the SFC method. IFSS test specimens were prepared as follows. A CF monofilament was fixed on the modified PP film by craft tape and sandwiched by another modified PP film. These fiber sandwiched films were pressed at 220 °C for 2 min under 0.1 MPa pressure by using a 37-t hydraulic press machine. They were then cooled to 50 °C under the same pressure, and a CF embedded sheet was obtained. A dumbbell-shaped specimen was cut from the sheet (stripe part width: 4 mm; length: 16 mm; and thickness: 0.5 mm). After tensile testing (crosshead speed: 4%/min), the fragmented fiber length (L_f) was measured using a digital microscope (Keyence Corporation; VHX-500). The average fiber fragment length (L_{af}) was calculated from L_f, and the number of fragments (L_n) was calculated by Equation (2). Then, the critical fiber length (L_c) and IFSS (τ) were, respectively, calculated by Equations (3) and (4).

$$L_{af} = \frac{\sum L_f}{L_n} \quad (2)$$

$$L_c = \frac{4}{3} L_{af} \quad (3)$$

$$\tau = \frac{\sigma_f \cdot d}{2L_c} \quad (4)$$

The fracture surface after the Izod impact test was observed using a scanning electron microscope (SEM). The fracture surface was coated with Pt as observed by FE-SEM (Hitachi High-Technologies; S-4800; accelerating voltage: 10.0 kV).

3. Results and discussion

3.1. Injection-molded products

Figure 2 shows the relationship between the IFSS and the acid-modified PP content. The IFSS doubled upon the addition of a small amount of acid-modified PP (10%); however, only a gradual increase was observed in case of 100% of acid-modified PP. This result reveals the quantitative relationship between the acid-modified PP content and IFSS. It also shows that the IFSS can be quantitatively controlled simply by changing the acid-modified PP content in the matrix resin.

Injection-molded specimens were prepared by using these matrix resins (acid-modified PP content in matrix: 0, 10, and 100%), and their mechanical properties were tested (Table 1).

With regard to the matrix resins, homo PP shows better mechanical properties, especially in the Izod impact strength tests. CFRPs (Vf = 5.3%) exhibited higher bending strength and modulus.[9,10] CFRPs with homo PP showed decreased Izod impact strength compared to the matrix resin (Run 1). On the other hand, CFRPs with acid-modified PP showed much higher Izod impact strength compared to the matrix resin (Run 3).

Figure 3 shows the fiber length distribution of the specimens used in Runs 1 and 3. The average fiber length of the respective specimens was 0.35 and 0.33 mm. CF was broken by a melt-mixing and injection process. No significant difference in fiber length was observed in each specimen. These results indicate that the Izod impact strength of

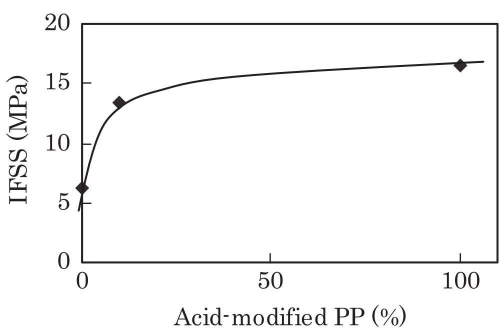


Figure 2. Relationship between IFSS and content of acid-modified PP.

Table 1. Mechanical properties of matrix resins and injection-molded products.

			Matrix resin			Injection-molded product				
Run no.	Resin [wt.%]		Bending strength [MPa]	Bending modulus [GPa]	Izod impact strength [kJ/m^2]	Vf [%]	Bending strength [MPa]	Bending modulus [GPa]	Izod impact strength [kJ/m^2]	IFSS [MPa]
1	Homo PP Acid-modified PP	100 0	57	2.0	3.5	5.3	90.6	5.2	2.7	6.21
2	Homo PP Acid-modified PP	90 10	58	1.9	2.6	5.3	102	5.2	3.9	13.31
3	Homo PP Acid-modified PP	0 100	53	1.7	2.4	5.3	99.7	5.0	5.0	16.59

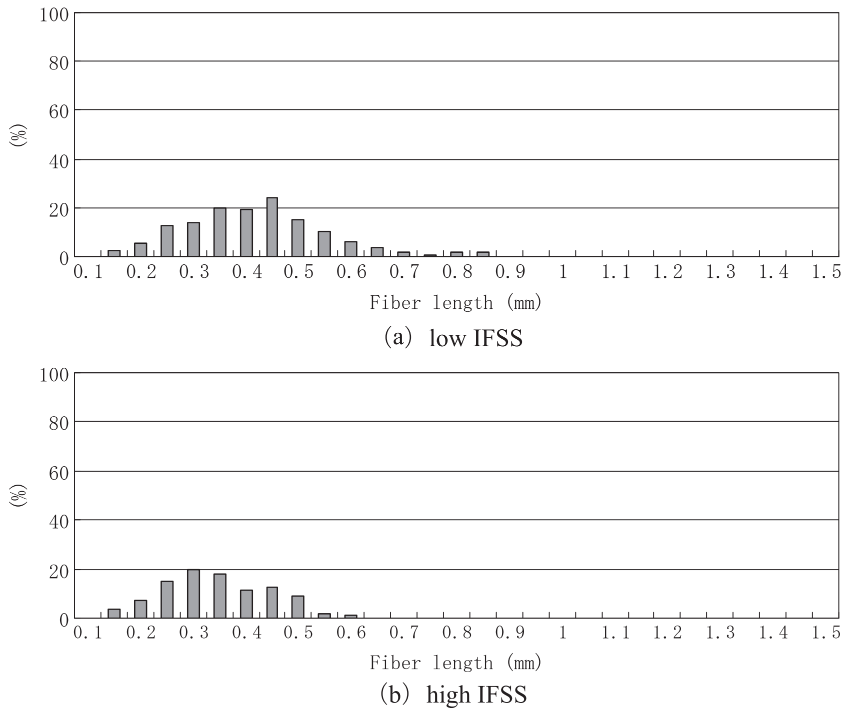


Figure 3. Fiber length distribution of injection-molded samples.

CFRP was improved by increasing the CF/PP adhesion. The effect of the IFSS on the bending and Izod impact strength is shown in Figure 4. The bending strength saturated when the IFSS reached 13.3 MPa (Run 2). The slight decrease in bending strength in Run 3 is due to the matrix resin properties. These data indicate that the breakage mode shifts from interfacial debonding at lower IFSS to matrix breakage at higher IFSS. The Izod impact strength simply increased with the acid-modified PP content. Therefore, the impact strength is controlled by interfacial adhesion in this IFSS range.

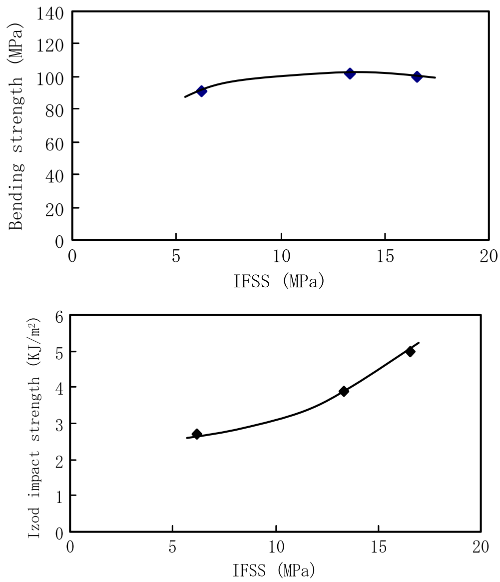


Figure 4. Comparison of bending strength and Izod impact strength vs. IFSS (injection molded product).

3.2. CFRP sheet

The bending strength and Izod impact strength of the CFRP sheet (Vf = 20%) are shown in Table 2. The bending strength saturated at higher IFSS in injection-molded products. On the other hand, the Izod impact strength exhibited the opposite tendency from that shown in Table 1. CFRPs with homo PP showed the highest impact strength (43 kJ/m^2, Run 4), whereas those with acid-modified PP showed reduced strength.

Figure 5 shows the fiber length distribution of the specimens used in Runs 4 and 6. The average fiber length of the respective specimens was 4.04 and 4.12 mm. The fiber length was maintained compared to that of the injection-molded product because the CFRP sheet in this case was made by impregnating a melted resin by pressing, and CF breakage was limited. The fiber length in the case of Runs 4 and 6 showed a difference that was negligible from the viewpoint of the mechanical properties.

Figure 6 shows the relationship between the bending strength or Izod impact strength and the IFSS. The bending strength showed the same tendency as that of the

Table 2. Mechanical properties of unidirectional CFRP sheets.

			CFRP sheet			
Run no.	Resin [wt.%]		Vf [%]	Bending strength [MPa]	Bending modulus [GPa]	Izod impact strength [kJ/m^2]
4	Homo PP	100	20	218	12.5	43
	Acid-modified PP	0				
5	Homo PP	90	20	316	14.1	16
	Acid-modified PP	10				
6	Homo PP	0	20	305	13.6	9.9
	Acid-modified PP	100				

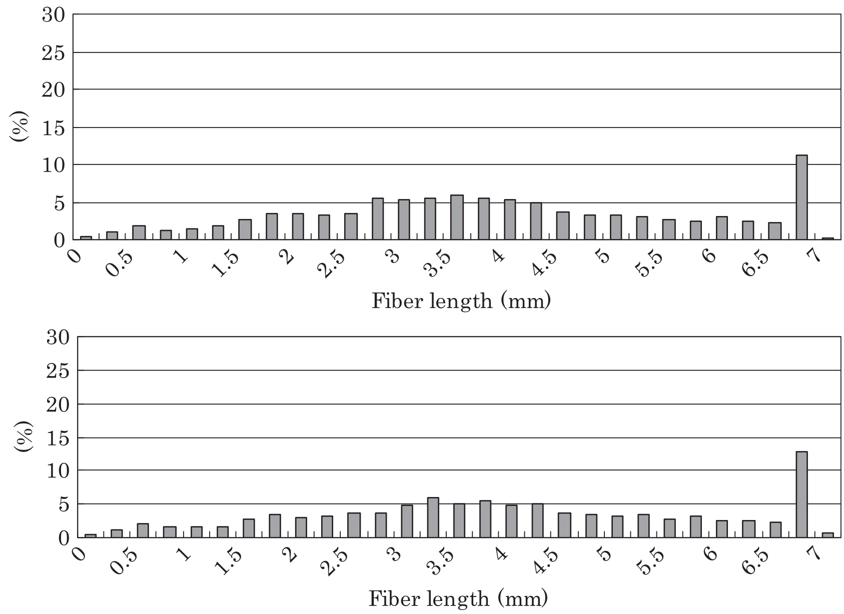


Figure 5. Fiber length distribution of press-molded samples.

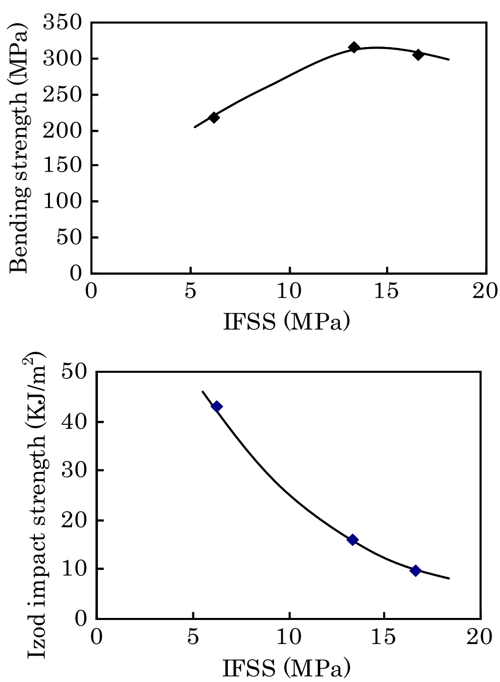
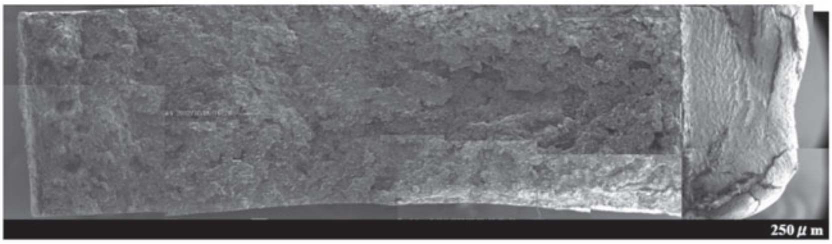


Figure 6. Comparison of bending strength and Izod impact strength vs. IFSS (press-molded product).

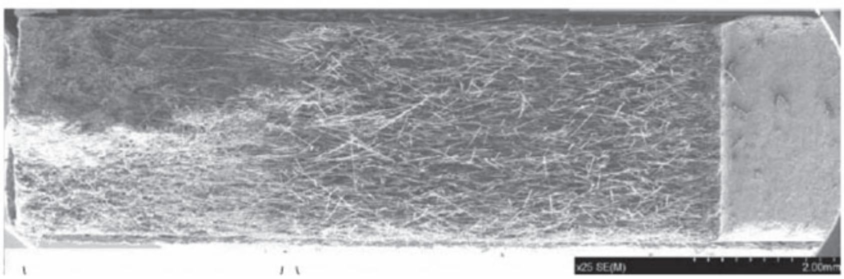
injection-molded products (Figure 4). However, the Izod impact strength showed a completely opposite trend, and a lower IFSS led to higher impact strength.

Figure 7 shows SEM images of the fracture surfaces of the Izod specimens used in Runs 1, 3, 4, and 6. In the Izod impact test, a tensile load was added at the notch side (right-hand side in the photograph) and a compression load was added at the opposite side (left-hand side in the photograph). No significant difference was observed between the injection-molded specimens (Runs 1 and 3). In the case of the CFRP sheet, an

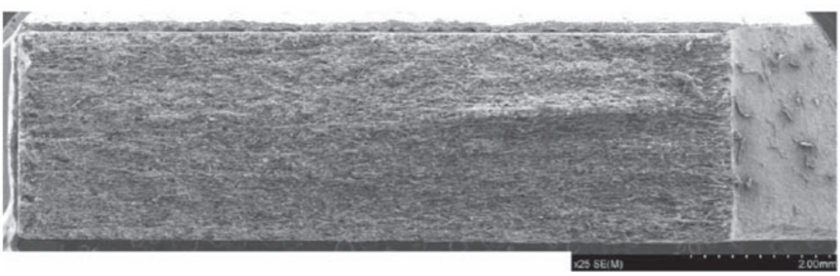


(a) Run 1 (low IFSS)

(b) Run 3 (high IFSS)



(c) Run 4 (low IFSS)



(d) Run 6 (high IFSS)

Figure 7. Fracture surfaces of Izod impact test specimens.

obvious difference was observed at the tensile side. The fracture surface was covered with pulled out CF from the notch side to the middle of the low-IFSS specimen used in Run 4. This indicates that CF was pulled out from the matrix resin without breakage owing to low CF/PP adhesion. In the high-IFSS specimen used in Run 6, the fracture surface was almost flat.

Figure 8 shows a magnified image of the middle of the fracture specimens. Less matrix resin sticking was observed on the CF surface in the low-IFSS sample. Additionally, a narrow space was observed at the root of the CF in the low-IFSS sample. These

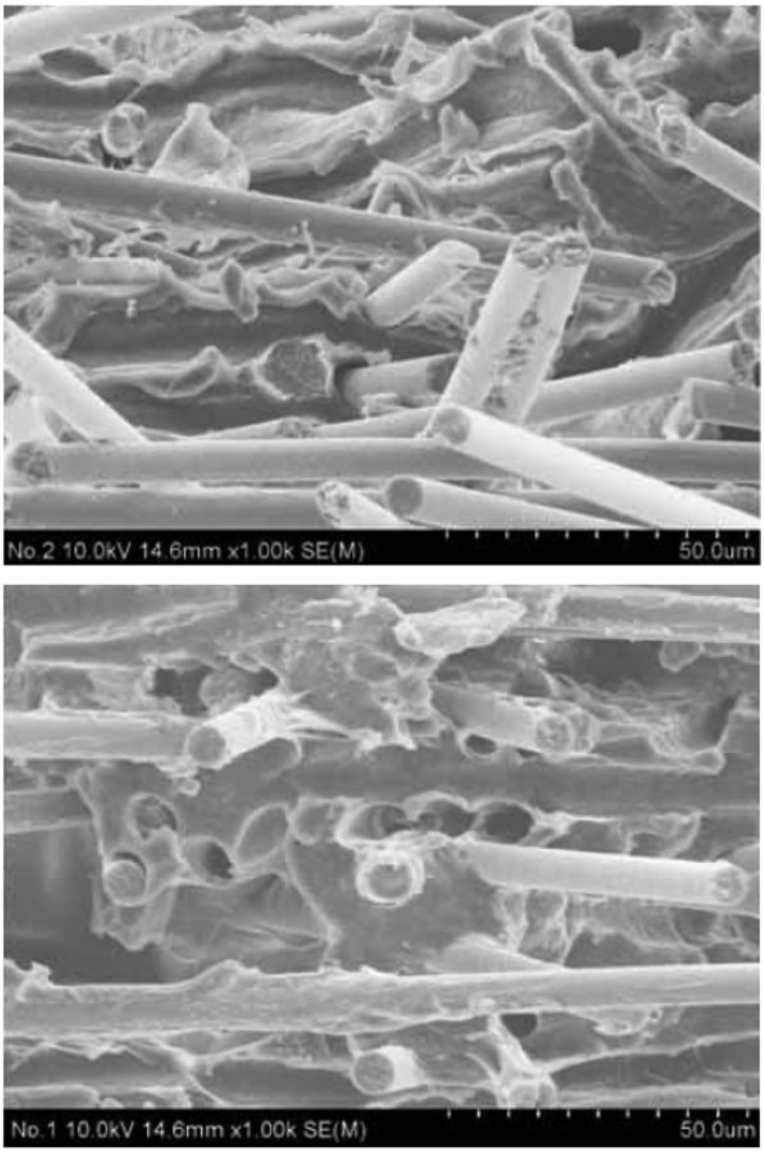


Figure 8. Magnified SEM image of fracture surfaces of Izod impact test specimens. (top: Run 4 (low IFSS), bottom: Run 6 (high IFSS)).

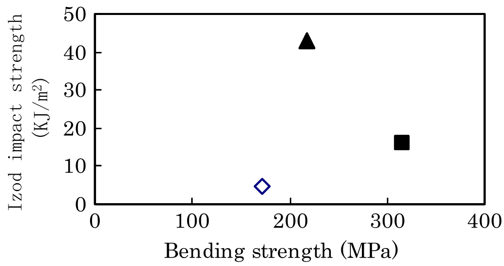


Figure 9. Comparison of Izod impact strength vs. bending strength for molded product, unidirectional CFRP sheet with high IFSS, and unidirectional CFRP sheet with low IFSS (Vf = 20%). ◆: injection-molded product (high IFSS), ■: CFRP sheet (high IFSS), ▲: CFRP sheet (low IFSS).

might be caused by low adhesion between the CF and the matrix resin. In the high-IFSS samples, some matrix resin sticking was observed on the CF surface, and the resin was observed to rise around the root of the CF. These fracture surfaces indicate that a low-IFSS sample absorbs much energy via CF pull out from the matrix resin and exhibits higher impact strength.

These results also explain the difference between the impact strength tendencies of injection-molded products and CFRP sheets. When the fiber length was short, the energy absorption due to pull out was not sufficient owing to the smaller surface area. Therefore, IFSS dominates the Izod impact strength in injection-molded products.

Finally, we compared the mechanical properties of the injection-molded product and the CFRP sheet for the same Vf (20%) (Figure 9). The CFRP sheet showed higher impact strength than that of the injection-molded product in the same matrix resin. This is due to the fiber length effect. When a technique for controlling the IFSS was applied, the impact strength increased to around nine times that of the injection-molded product while the higher bending strength was maintained.

4. Conclusion

In this study, we quantitatively discussed the relationship between the PP composite properties and IFSS. The following conclusions can be drawn from our obtained results.

(1) IFSS was quantitatively controlled by changing the proportion of acid-modified PP in the matrix resin.
(2) Both injection-molded products and CFRP sheets showed the same tendency with regard to the bending strength. The bending strength increased with increasing IFSS and saturated at high IFSS.
(3) The injection-molded product showed higher impact strength when the IFSS increased, whereas the CFRP sheet showed higher impact strength when the IFSS decreased. This is because the CFRP sheets have longer CFs that absorb much more energy upon CF pull out.
(4) By controlling the IFSS, a CFRP sheet having around nine times the impact strength of an injection-molded product was obtained.

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