Effect of Water Absorption on the Mechanical Properties of Carbon Fiber/Polyamide Composites*

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Abstract

Polyamide (PA) resin is anticipated to be a beneficial matrix of carbon fiber reinforced thermoplastics (CFRTP) because of its low cost and good bonding property to the carbon fiber. However, the well-known highly hygroscopic nature of PA demands that the influence of water absorption on the mechanical properties of carbon fiber/polyamide composites (CF/PA) be clarified. In this study, to evaluate the influence of water absorption on the mechanical properties of CF/PA composites, single fiber pull-out test for CF/PA model composites and tensile test for CF/PA composite were performed. For CF/PA6, and CF/PA66 model composites, water absorption at 80 °C caused significant reductions in interfacial shear strength. CF/PA12 model composites also showed a decrease in interfacial shear strength due to water absorption, but to a smaller degree compared with that of the other model composites tested. Oven drying was able to completely reverse the deleterious effect of water absorption on the interfacial shear strength in CF/PA6 and CF/PA12 model composites, but full restoration was not possible in CF/PA66 model composites. Oven drying was able to restore tensile strength in CF/PA6, CF/PA12 and CF/PA66 composites.

Key words: Polyamide, Carbon Fiber, Interfacial Shear Strength, Thermoplastics, Water Absorption, Transcrystal

1. Introduction

The reduction of vehicle weight is a primary method for improving automobile fuel economy. The use of Carbon Fiber Reinforced Plastic (CFRP), one of a number of solutions for reducing weight in automotive applications, requires specific focus on manufacturing and cost. For CFRP used in aerospace structures and certain advanced sports cars, thermosetting epoxy resins are widely employed as matrix materials. However, since thermoset plastic cannot be melted and reshaped after curing, they are not well-suited for mass-produced vehicles that increasingly require the use of recyclable materials ^(1, 2). Thus, thermoplastic matrix materials are indicated when employing CFRP in mass-produced automotive parts, due to their recyclability, ease of production, and resistance to impact. The use of continuous carbon fiber as a reinforcing material increases the advantages offered by Carbon Fiber Reinforced Thermoplastics (CFRTP) and research on CFRTP forming method has advanced considerably ^(3~6). In our previous study, a high-speed

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compression molding system employing a Non-woven Stitched Multi-axial Cloth (NSMC) was developed ^(7, 8). In the case of this high-speed forming, the ecological manufacturing process of a continuous carbon fiber reinforced thermoplastics can be achieved. Comprehensive evaluation of the mechanical properties of continuous carbon fiber reinforced thermoplastics is thus necessary for the further development of CFRTP application.

Comparatively inexpensive resins such as polypropylene (PP) and polyamide (PA) ^(9, 10) are considered appropriate matrix materials for CFRTP in mass-produced automotive parts. PA polymers are particularly suitable from the viewpoint of recycling and bonding property with carbon fiber ⁽¹¹⁾, but PA6 is very hygroscopic, so the influence of water absorption on the mechanical properties of CF/PA composite must be clarified. Pillay ⁽¹²⁾ evaluated the effect of water absorption upon CF/PA continuous fiber composites, using a bending test, but earlier studies are mainly concerned with short fiber reinforced composites. Since different PA formulations, such as PA6, PA12 and PA66, are used for particular purposes, examination of the effects of water absorption on the properties of PA resin composites must include a variety of PA matrix materials.

Macroscopic fracture tests are generally used to evaluate environmental degradation, but environmentally induced degradation of composites has not been fully clarified due to the complex fracture modes involves, such as fiber breakage, matrix fracture, delamination, fiber bridging and fiber/matrix interfacial debonding. Therefore, the influence of environmental factors on individual components of composites, such as fibers and matrix, as well as the fiber/matrix interface must be investigated. So far, investigation using model composites for carbon and aramid fibers embedded in thermosetting resin has been done to evaluate degradation of fiber/matrix interface ^(13, 14), but there are few studies concerning the fiber/matrix interfacial properties in thermoplastic matrix materials.

In this study, single fiber pull-out tests were carried out to evaluate the interfacial properties of CF/PA model composites for PA6, PA12 and PA66, and quantitative assessment of degradation due to water absorption was conducted. In addition, CF/PA composites were molded by high-speed compression molding process and mechanical properties of CF/PA composites were evaluated to verify the effect of the water absorption.

2. Experimental procedure

2.1. Material and specimen preparation

Polyamide6 (PA6), Polyamide12 (PA12) and Polyamide66 (PA66) were melt-blown to a non-woven fabric (Prototype; Kuraray Co., Ltd, Japan) in the weight per unit area of 50 g/m² and neat resin specimens were molded by press molding.

PAN-based carbon fibers (Standard grade, Tensile modulus: 240GPa, Fiber diameter: 7 μm) were used for the single fiber pull-out test. Figure 1 shows a schematic illustration of the specimen preparation. After a single fiber was glued to a tab with adhesive, the tab was attached to micromanipulator. The free fiber length was about 3 mm. PA resin was placed on the aluminum plate heated to 250 °C for PA6, 220 °C for PA12 and 300 °C for PA66, and the micromanipulator was used to insert the end of the single fiber into the melted resin. After the designed length of fiber was embedded in the resin, the resin was air-cooled. These specimens are referred to as CF/PA model composite and these CF/PA model composites will be used for single fiber pull-out tests to evaluate the effect of water absorption on the fiber/matrix interfacial properties.

The CF/PA composites were molded using a high-speed compression molding process ⁽⁷⁾ for tensile specimens. NCF (Non-Crimp fabrics) of carbon fiber (0°/90°) with the weight per unit area of 200 g/m² were used for the reinforcement and non-woven fabrics of PA6, PA12 and PA66 were used for the matrix. The fiber volume fraction for the specimens was set at 50 %. The molding conditions for the specimens are listed in Table 1. Thickness of the

CF/PA composites were 1 mm and the CF/PA composites were cut into 10×170 mm by water-jet machining. These CF/PA composites are employed to evaluate the effect of water absorption on the mechanical properties of composites.

The single fiber embedded specimens were also molded as shown in Fig. 2 using the same molding condition as for the CF/PA model composite specimens. The single fiber embedded specimens were observed using a polarizing microscope (Olympus Optical Ltd, BH-5) to observe the resin in the interfacial regions.

Fig. 1 Shapes and dimensions of CF/PA model composite for pull-out tests.

Fig. 2 Schematic drawing of a single fiber embedded specimen.

Table 1 Molding condition for CF/PA composite specimens.

	Temperature [°C]	Pressure [MPa]	Molding time [s]
CF/PA6	250	2	60
CF/PA12	220	4	90
CF/PA66	300	2	60

2.2. Water absorption test

Water absorption tests for PA neat resins and CF/PA composites were performed to assess the amount of absorbed water as a function of immersion time. PA neat resins and CF/PA composites were cut into 10×20×1 mm specimens that were immersed in distilled water at 80 °C. The specimens were periodically weighted after excess moisture was wiped off and the percentage of weight gain was monitored as a function of the square root of time, using the following equation.

$$C = (m - m_0) / m_0 \times 100 \quad (1)$$

where C is the percentage weight gain, m is the weight of the specimens including absorbed water at a specific time, and m_0 is the dry weight

Some specimens of CF/PA composites and CF/PA model composites were immersed in distilled water at 80 °C for 100 hours, and others were kept in laboratory air. These specimens will be referred to as wet (100h) and dry, respectively. After 100 hours of immersion in water, some specimens were dried in an oven at a constant temperature of 100 °C for 24 hours. These specimens will be referred to as re-dried specimens.

2.3. Pull-out test

Pull-out tests were performed for CF/PA model composites using an electrohydraulic servo controlled testing machine for micro material (MMT-11N, Shimadzu Corp. Japan). After chucking a specimen with a pin hole of the tab, the supporting part of the tab was cut and the pull-out test was conducted using a constant displacement rate of 1.67×10^{-6} mm/s (0.1 mm/min). Embedded fiber lengths were precisely measured after the pull-out tests using scanning electron microscope (JSM-6390LT, JEOL Ltd., Japan).

2.4. Tensile test of CF/PA composites

The tensile tests were conducted for CF/PA composites using a universal testing machine (Autograph AG-100kNX, Shimadzu Co., Japan) and a video non-contact extensometer (DVE-201, Shimadzu Co., Japan) for measuring the extension of specimen, following the recommended testing procedures described in JIS-K7164. Fracture surfaces were observed using the SEM.

MFR (Melt mass-Flow Rate) of PA6, PA12 and PA66 were measured using a meltindexer to evaluate resin material flowability, following the recommended testing procedures described in JIS-K7210. A 2.16 kg measurement load and a dwell-time of 6 minutes were used.

3. Results and discussion

3.1. Water absorption property

Figures 3 show the water absorption curves for the tested PA resins and CF/PA composites. For PA resins, after a rapid increase, the amount of water absorbed reached a maximum value (PA6, 8.3 %; PA12, 1.5 %; PA66, 7.2 %), and then decreased slightly. PA12 absorbed the least amount of water, roughly one-fifth that of PA6 and PA66. The number of amide groups in polyamide resin molecules affected their water absorption characteristics. Therefore, PA6 and PA66 showed relatively high percentage of absorption, but PA12, with fewer amide groups than the others, had the lowest water absorption rate. It is widely reported that PA resin is degraded by water absorption; and in comparison to PA6 or PA66, PA12 is better in tolerance to water absorption. These tendencies are reflected in the water absorption curves for the CF/PA composites shown in Fig.3. Consequently, it can be said that CF/PA12 composites are more resistant to water absorption than the other composites tested.

(a) PA resin.

(b) CF/PA composite.

Fig. 3 Water absorption curves.

3.2. Pull-out test

The interfacial shear strength, τ , was calculated by the following definition.

$$\tau = \frac{F_{\max}}{\pi dl} \quad (2)$$

where $F_{\max}$ represents the maximum load required to pull out the carbon fiber from specimen, d is the fiber diameter and l is the embedded fiber length.

Figure 4 shows the summarized results of interfacial shear strength tests for wet, re-dried, and dry specimens. For CF/PA6 model composites, the interfacial shear strength of dry specimens was 39.2 MPa, and that of wet(100 h) specimens was 26.0 MPa, 66 % of the dry specimen value. For CF/PA12 model composites, the interfacial shear strength of dry specimens was 41.2 MPa, and that of wet(100 h) specimens was 33.4 MPa, indicating a reduction to 84 % of the dry specimens value. Although the interfacial shear strength was decreased by water absorption, the ratio of decrease in CF/PA12 model composites was smaller compared with that of the other model composites, indicating that the PA12 interface area has superior resistance to degradation in aqueous environments. For CF/PA66 model composites, the interfacial shear strength of dry specimens was 59.5 MPa, and that of wet(100 h) specimens was 31.3 MPa, a reduction to 53 % of the dry specimen value. Thus the effect of water absorption on the interfacial shear strength in CF/PA66 model composites was more severe than that observed in other model composites.

Our tests showed that re-drying the CF/PA6 and CF/PA12 model composites in an oven was able to reverse the deleterious effect of water absorption on interfacial shear strength, but recovery was incomplete in CF/PA66 model composites. The recovery observed in CF/PA6 model composites, despite a one-third reduction in interfacial shear strength due to water absorption, was particularly noteworthy. Our results suggest that the mechanism responsible for interfacial shear strength reductions may be different depending on the combination of fiber and resin materials.

Figure 5 shows micrographs of interface area in single fiber embedded specimens. Optical polarizing microscopy revealed significant differences in the columnar structures surrounding the carbon fiber in the CF/PA6 and CF/PA12 single fiber embedded specimens shown in Figs. 5(a) and (b). As in many reinforced semicrystalline thermoplastics, an interphase composed of transcrystalline region developed due to the high nucleation density of the polymer on the fiber surface^(15, 16). Transcrystal have been previously observed on CF/PA6 single fiber embedded specimens⁽¹⁷⁾. The columnar structures surrounding the carbon fiber in Figs. 5(a) and (b) can be recognized as transcrystals. However, in CF/PA66 single fiber embedded specimens, change in the resin in the interfacial neighborhood is not observed, as shown in Fig. 5(c).

Since water molecules combine easily with the amide radical in amorphous regions, and transcrystals are formed in the interface regions in CF/PA6 and CF/PA12 single fiber embedded specimens, water molecule was hardly absorbed at the interface region. This suggests that the measured reductions in interfacial shear strength are due to changes in the properties of resins in a domain beyond the fiber/matrix interface. For CF/PA66 model composites, the interfacial shear strength of re-dried specimens that were previously degraded by absorbed water does not reach that of dry specimens that were not exposed to water. This suggests that in the exposed specimens, in addition to changes in matrix properties, there are additional interfacial bond failures that are irreversibly caused by water absorption, namely, hydrolysis reactions.

Fig.4 Fiber/matrix interfacial shear strengths.

Fig.5 Micrographs of single fiber embedded specimens.

3.3. Tensile test

Figure 6 shows the summarized results of tensile tests for wet specimen, re-dried, and dry specimens. The results of MFR measurement for PA6, PA12 and PA66 are shown in Table 2. The dry CF/PA6 and CF/PA66 composite specimens were almost equal in tensile strength, but the dry CF/PA12 composite had a lower value. The MFR of PA12 was smaller than that of other specimens. These results indicate that resin impregnation was not completed due to the higher viscosity of PA12. For CF/PA6 and CF/PA66 composites, water absorption caused reductions in tensile strength but this was not the case for CF/PA12 composites after exposed to water at 80 °C for 100h. As shown in Fig.4, for CF/PA12 model composites, relatively smaller decrease in interfacial shear strength due to the water absorption was observed. This smaller decrease may be correlated with the smaller decrease

in tensile strength.

Figure 7 shows SEM images of typical fractures in CF/PA6, CF/PA12, and CF/PA66 composites, for dry and wet (100h) specimens. In dry CF/PA6 composite specimens, fiber surfaces are covered with resin, indicative of good fiber/matrix interfacial strength. In contrast, wet CF/PA6 composite specimens reveal many exposed fiber surfaces. These results indicate a possible correlation between decreased fiber/matrix interfacial strength due to water absorption and the deterioration in the tensile strength of CF/PA6 composites. On the other hand, both wet and dry CF/PA12 composite specimens showed fiber surfaces covered with resin. Briefly, interfacial strength was maintained after water absorption, and deterioration in tensile strength was suppressed in CF/PA12 composites. Last, for CF/PA66 composites, exposed fiber surfaces were observed for wet specimens, and similar behavior to that of CF/PA6 composites was observed.

For all CF/PA composite specimens tested, the obtained tensile strength of re-dried specimens was almost equal to that of specimens not exposed to water. As shown in Fig.4, for CF/PA6 and CF/PA12 model composites interfacial shear strength was recovered by oven drying, but the recovery for CF/PA66 model composites was not completed. However, the obtained interfacial shear strength of re-dried CF/PA66 model composites was almost equal to that of dry CF/PA6 and CF/PA12 model composites. This indicates that the obtained value for interfacial shear strength of re-dried CF/PA66 model composites is enough to show the tensile strength of composites.

Fig.6 Tensile strength.

Table 2 MFR results.

	Temperature [°C]	MFR [g/10min]
PA6	250	129.5
PA12	220	53.4
PA66	300	235.9

Fig.7 SEM micrographs for fracture surface of CF/PA composites.

4. Conclusions

Single fiber pull-out tests were carried out to evaluate the interfacial properties of CF/PA model composites, and quantitative assessment of degradation due to water absorption was conducted. In addition, the mechanical properties of CF/PA composites were evaluated. Our investigation yielded the following conclusions:

- (1) For CF/PA6 and CF/PA66 model composites, absorption of water at 80°C caused significant reductions in interfacial shear strength. CF/PA12 model composites showed a similar decrease in interfacial shear strength, but to a lesser degree.
- (2) For CF/PA6 and CF/PA12 model composites, the deleterious effect of water absorption on interfacial shear strength was reversed by oven drying. In contrast, for CF/PA66 model composites, interfacial shear strength was not completely restored by oven drying. The absence of transcrystals in CF/PA66 is responsible for this difference.
- (3) For all CF/PA composite specimens tested, the obtained tensile strength of re-dried specimens was almost equal to that of specimens not exposed to water.

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