INFLUENCES OF WATER ABSORPTION ON THE MECHANICAL PROPERTIES OF DISCONTINUOUS CF/PA6 AND CF/PP

H. Piao*1, Y. Kiryu1, L. Chen1, S. Yamashita1, H. Wei1, I. Ohsawa1 and J. Takahashi1

1Department of Systems Innovation, The University of Tokyo, Tokyo, Japan
*Email : piao-hao@cfrtp.t.u-tokyo.ac.jp, Web page : http://j-t.o.oo7.jp/index-e.html

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Abstract
Carbon fiber reinforced thermoplastics (CFRTP) show relatively high mechanical properties and have been expected as feasible material for light-weight structures in mass-production. Especially, discontinuous CFRTP (DCFRTP) with affordable resins have been developed to realize excellent formability and mechanical properties. Currently, polyamide 6 (PA6) is expected as the matrix of CFRTP for mass-produced automobiles. However, due to the hygroscopic property of the polyamide resin and the discontinuous morphology of DCFRTP, the influence of water absorption on their mechanical properties should be investigated. In this study, influences of water absorption on the mechanical properties of discontinuous CF/PA6 composites were investigated. Chopped carbon fiber tape reinforced thermoplastics (CTT) and carbon fiber paper reinforced thermoplastics (CPT) were selected as DCFRTP materials. The mechanical properties of the composites are investigated by three point bending test from -40 degrees Celsius to room temperature. The mechanical properties of both CTT and CPT present relatively high sensitivity on the water absorption.

1. Introduction

Carbon fiber reinforced plastics (CFRP) show relatively high mechanical properties and have been expected as feasible materials for light-weight structures [1, 2]. However, the low productivity and relatively high cost hinder the application of CFRP in mass-production. In order to solve this issue, carbon fiber reinforced thermoplastics (CFRTP) have been developed to realize excellent formability and mechanical properties [3]. Specifically, discontinuous CFRTP (DCFRTP) have merits in decreasing the production cost and render additional routes to apply discontinuous CF, which also includes current available recycled carbon fibers (RCF).

Currently, polypropylene (PP) and polyamide 6 (PA6) are expected as the matrix of CFRTP for mass-produced automobiles. PA6 is comparatively more suitable because of its promising adhesion property with carbon fiber (CF). However, there is concern about the effect of water absorption on the properties of PA6 in actual application. Despites the hygroscopic property of the polyamide resin, the discontinuous morphology of DCFRTP make it necessary to clarify the influence of water absorption on their mechanical properties. Furthermore, in automotive application, the operating temperature range is very high in summer and very low in winter. Therefore, the investigation of the influence of water absorption together with the operating temperature is even more necessary.

Since the beginning of mass production of nylon, some studies of PA composite materials have been conducted [4-9]. Most of them focused on characteristics of hygroscopic property and temperature dependence. Taktak et al. [4] quantified the effect of water absorption rate on tensile properties of PA6. In their conclusion, the yield stress of PA6 shows temperature dependence with water absorption.

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Tanaka et al. [5] reported that the interfacial adhesion property between the carbon fibers and resin was decreased by the water absorption of PA6. The motility of water molecules in carbon fiber reinforced composite with PA6 has been examined by Kawagoe et al. [6]. The water molecules were presented as non-freezing water bonding to the amide group. In addition, the report also showed that the presence proportion of the moving water increased with complexation of fiber package in composites at a low temperature. Influence of water absorption on the flexural properties of glass fiber reinforced PA66 composite was investigated by Valentin et al. [7]. A reduction in mechanical properties due to water absorption of resin was shown to be remarkable for discontinuous fibers. Monte et al. [8] concluded that the operating temperature and the specimen thickness have great influence on the out-of-plane tensile properties of glass fiber reinforced PA66 composite. They also illustrated that the influence of specimen thickness should be taken into the consideration including the temperature dependence of the tensile properties. Nagatsuka et al. [9] investigated the temperature and time dependence of DCFRTP with PP. The temperature dependence is strongly reflected in the mechanical properties of DCFRTP.

Although a lot of researches have investigated the effects of temperature dependence and the water absorption on the mechanical properties of CFRTP, the studies of these two types of effects are still insufficient related to DCFRTP. Moreover, most researches mainly focused on temperature dependence at high temperature range. However, it is also necessary to take into consideration of the effect of low temperature range, which is under the water freezing, on the water absorption of CFRTP.

Furthermore, the intrinsic structures of DCFRTP are thought to be a combinational factor affecting the described two environmental factors: water absorption and temperature dependence. In multidirectionally reinforced composites which is composed of discontinuous carbon fibers, there are randomly orientated filaments and in-plane dispersed chopped fiber tapes. In this study, influences of water absorption on the mechanical properties of chopped carbon fiber tape reinforced thermoplastics (CTT), which is a kind of randomly oriented strand (ROS) composites, and carbon fiber paper reinforced thermoplastics (CPT) are investigated by discussing the mechanical properties by three point bending test from -40 degrees Celsius to room temperature.

2. Materials and experiment

2.1. Materials

An ultra-thin unidirectional CF/PA6 preimpregnated sheet was used to make CTT in the present study. This sheet was manufactured by Industrial Technology Center of Fukui Prefecture using tow spreading technology [10]. The thickness is 44 μm and the volume fraction of CF (V_f) is about 55%. CF was manufactured by Mitsubishi Rayon Co., Ltd, and PA6 was manufactured by Mitsubishi Plastics, Inc. The sheet was cut by an automated tape cutter and Tomson cutter into chopped tapes with 18 mm in length and 5 mm in width. The chopped tapes were dispersed by wet dispersion process and the dispersed tapes are briefly heated and compressed to make fixed and portable sheet of the size of 250 mm × 250 mm. The detail of this fabrication process can be viewed in a previous study [11]. This procedure can prevent tapes from misorientation in out-of-plane direction. In order to highlight the ultra-thin thickness of the CTT, it is also called UT-CTT (ultra-thin carbon fiber tape reinforced thermoplastics).

CPT material was manufactured from CARMIX® [12] made by Awa Paper Mfg. Co., Ltd. CARMIX sheet used in this study is composed of CF and PA6 fiber dispersed by a continuous paper-making process. The average length of CF and PA6 fiber are closed to 6 mm. The V_f is about 24%.

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2.2. Specimen preparation

Composites specimens were prepared by compression molding. Thickness of specimens could be variable by changing the number of temporarily fixed sheets and, in this study, it was fixed to 3 mm. The temperature of the mold was heated up to 255 degrees Celsius. Molding pressure was 1 MPa at the first stage for impregnating and maintained 10 minutes. After preheating procedure, the pressure was increased up to 5 MPa and maintained 15 minutes for forming. At the final cooling stage, the molded plate was removed from the mold around 60 degrees Celsius. The molded plates were cut into the specimen size with 80 mm × 30 mm × 3 mm by a diamond disc cutter. The specimens were dried in the vacuum dryer at 90 degrees Celsius.

PA6 specimens were molded by injection molding for water absorption test in order to obtain a reference data. Manual type of injection molding machine (Hand Truder PM-1, Toyo Seiki) was used. The PA6 films were melting at 255 degrees Celsius in the melting cylinder for 2 minutes. After that, the melted polymer was injected into the mold and the mold temperature was maintained at 90 degrees Celsius. The specimens were cooled down around 80 degrees Celsius and removed from the mold. The specimen size was 80 mm × 10 mm × 2 mm. The specimens were dried in the vacuum dryer at 90 degrees Celsius.

2.3. Water absorption test

Water absorption tests for PA6 and composites were performed to assess the amount of absorbed water by immersion time. Before the water absorption tests, the weight of specimens was measured every 24 hours (1 day) during the drying process because the specimens cannot be used as sufficiently dried ones unless the weight change is no more than 0.001%. Thereafter, specimen was immersed in distilled water at 70 degrees Celsius. A dry oven (Drying Oven Kosumosu, ISUZU) was used to create an experiment environment with a constant temperature in order to keep the water temperature.

The percentage of weight gain was monitored with using Equation 1:

$$C = \frac{m - m_0}{m_0} \tag{1}$$

where, C is the weight change ratio, m is the weight of specimens including absorbed water, m_0 is the weight of dried specimens.

Additionally, the theoretical maximum weight change ratio of composite was calculated from Equation 2:

$$C_t = C_{PA6}(1 - V_f) \tag{2}$$

where, C_t is the theoretical maximum weight change ratio, C_{PA6} is the maximum weight change ratio of PA6 obtained by the water absorption test.

2.4. Three point bending test

To discuss the influence of water absorption on mechanical properties of DCFRTP, three point bending tests were conducted. A universal testing machine (AUTOGRAPH AGXplus, Shimadzu Co,.) with thermostatic chamber was used. The span of the supporters on the testing machine is determined by the thickness of the specimens with the span-to-thickness ratio of 16:1. The crosshead speed was 1 mm/min. Additionally, operating temperature was selected as -30, 21, 0 degrees Celsius. The failure part of specimens after three point bending test was observed by a digital microscope (VHX-1000, Keyence Co.).

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3. Results and discussion

3.1. Water absorption property

The theoretical maximum weight change ratio of composite was calculated as shown in Table 1. For both UT-CTT and CPT, C is lower than the theoretical value, C_t. It can be inferred that the multidirectional reinforcement structures potentially hindered the water absorption. Figure 1 shows the water absorption curves of the PA6, UT-CTT and CPT. For the matrix, PA6, the weight change ratio is saturated at maximum value (8.66%). The mass of UT-CTT and CPT increased rapidly within 48 hours and then varied a little in consequence. CPT absorbed more water than UT-CTT. This is probably attributed to the lower V_f in CPT and the intrinsic morphology of randomly dispersed filaments. In UT-CTT, it can be suggested that the unidirectionally orientated CF with higher V_f in one tape hindered the water absorption, which also appeared in the water absorption speed illustrated as the lower slope of the water absorption curves (see Figure 1). Hence, it can be concluded that UT-CTT has anti water absorption structure.

Table 1. The weight change rate of each type of specimens at saturation.

Specimen	Experimental result C [%]	Theoretical value C_t [%]
PA6	8.66 (C_{PA6})	-
UT-CTT	2.79	3.80
CPT	5.94	6.05

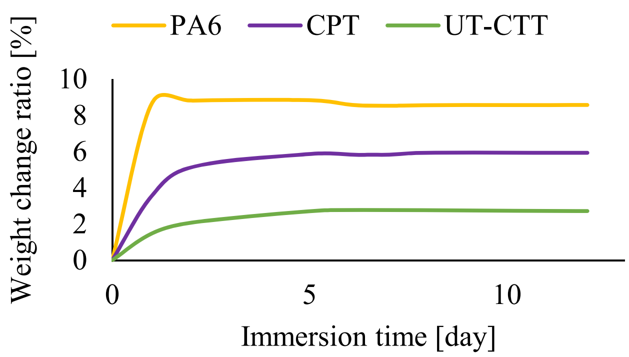

Figure 1. The changes in the weight change ratio of each type of specimens at 70 degrees Celsius.

3.2. Mechanical property

3.2.1 Influence of water absorption

The results of flexural modulus in dry and wet condition at the room temperature are shown in Figure 2. The flexural modulus of UT-CTT decreased by 17% and that of CPT decreased by 22%. According to Timoshenko's beam theory, the flexural modulus of composites is affected by longitudinal elastic modulus (E_1) and out-of-plane shear modulus (G_{13}) [13]. E_1 can be calculated from the tensile modulus and compression modulus, which are mainly depended on the elastic modulus and V_f of carbon fibers. On the other hand, G_{13} is a value that mainly depends on the mechanical properties of the matrix resin. Hence, G_{13} decreased probably due to decrease in the elastic modulus of the resin with water absorption [4, 14], and as a result, reduction of flexural modulus of DCFRTP were observed. CPT has

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higher reduction rate of the flexural modulus because the higher content of PA6 in CPT absorbed more water than UT-CTT, as shown in Figure 1.

The results of flexural strength are shown in Figure 2. The flexural strength of UT-CTT decreased by 41% after water absorption and that of CPT decreased by 34%. Water absorbed resin is known to reduce the interfacial adhesion between the CF and resin [5]. Furthermore, interfacial adhesion property contributes to the strength of the material in bending more significantly. As a result, both DCFRTP lose resistance potential to flexural stress after water absorption. In addition, larger reduction rate was observed in UT-CTT. The UT-CTT is composed of a number of layers of in-plane dispersed chopped tapes. As the basic structural units, CF tapes transfer the load within each other by the matrix. Even though the strength of one CF tape cannot be concluded to be decreased, the interface bonding between CF tapes are strongly weakened, which also allows the tapes to slide more easily during bending. The increased potential of tape sliding is also proved by Figure 3, in which undamaged CF tapes are found.

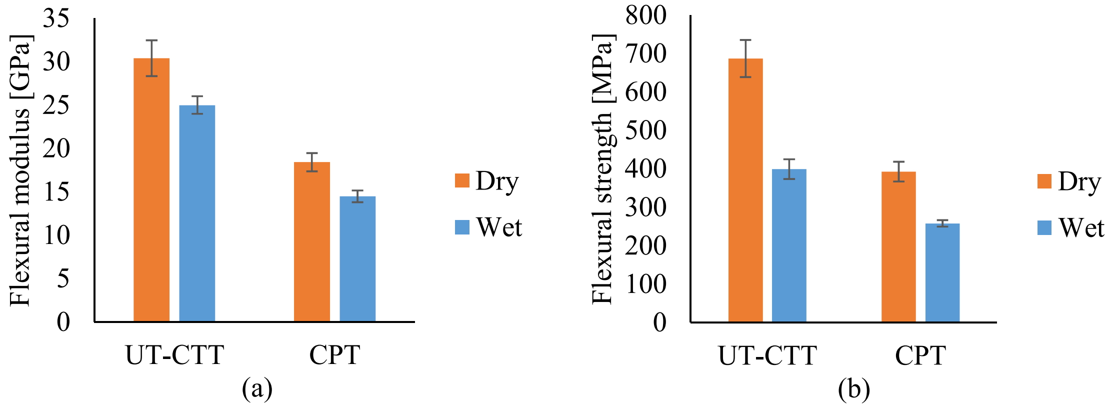

Figure 2. Comparison of flexural properties between dry and wet specimen at 21 degrees Celsius: (a) modulus and (b) strength.

Figure 3. Microscope observation on fracture part of UT-CTT: (a) dry and (b) wet.

3.2.2 Temperature dependence of DCFRTP

The both of dry DCFRTP showed temperature dependence slightly, as shown in Figure 4. On the other hand, the flexural modulus of water absorbed specimens showed more significant temperature dependence when the water became ice. It is known that mechanical properties of PA6 are varied by water molecules and environment temperature [4, 14, 15]. In addition, the degree of temperature dependence is different in dry state and wet state, that is, PA6 with water absorption shows larger change rate of flexural modulus due to temperature [15]. Hence, the flexural modulus of DCFRTP is affected by the operating temperature and the water absorption will enlarge the influence under 0 degrees Celsius.

As shown in Figure 5, flexural strength of UT-CTT increased when the temperature becomes lower in both case of dry and wet. The tendency was attributed to characteristics of PA6. Flexural strength of PA6 increases when the temperature becomes lower regardless of dry or wet [15]. For CPT, after water absorption, flexural strength found to be higher when the temperature decreases. In wet CPT, the result is also caused by temperature dependence of PA6 in flexural strength. However, the flexural strength decreased when the temperature becomes lower in dried specimens. Stress was transferred by a unit tape in UT-CTT, so the statistic effective length of CF is longer than that of CPT. On the other hand, stress transmission in CPT depends on fibers distributions. The randomly orientated CF in CPT combined with the lower V_f further weakened the resistance to failure. Furthermore at low temperature, the mobility of polymer molecule reduce and then materials became brittle. Thus, the failure strain of CPT was decreased from 0 degrees Celsius, as shown in Table 2. As a result, the flexural strength of dried CPT to decrease when the temperature became lower.

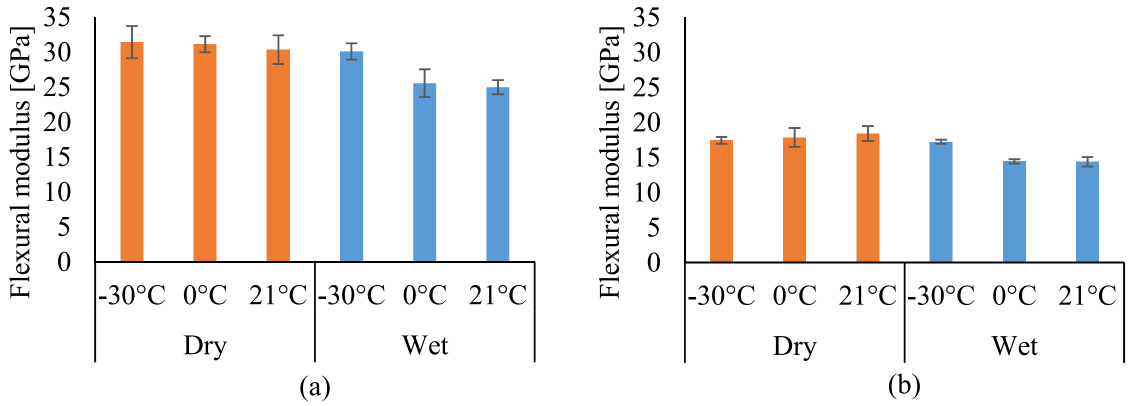

Figure 4. Flexural modulus at each testing condition: (a) UT-CTT and (b) CPT.

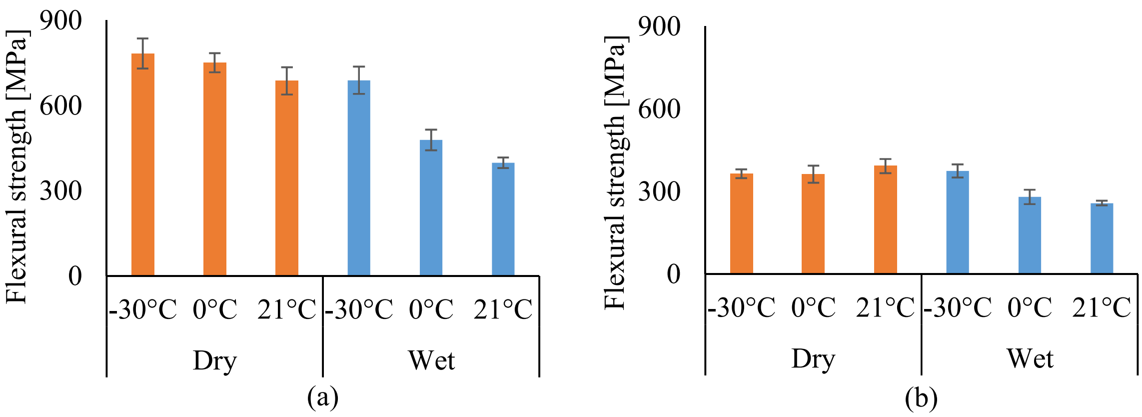

Figure 5. Flexural strength at each testing condition: (a) UT-CTT and (b) CPT.

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Table 2. Flexural strain at break for dried CPT at each condition.

Test temperature [°C]	Flexural strain at break (standard deviation) [%]
-30	2.07 (0.12)
0	2.02 (0.13)
21	2.21 (0.09)

4. Conclusions

In this study, water absorption properties of PA6, UT-CTT and CPT are investigated. The influence of water absorption on flexural properties of DCFRTP are also investigated. In addition, the temperature dependence of DCFRTP in flexural properties under low temperature range are discussed. The conclusions obtained in each investigations are as follows.

(1) Water absorption property:
According to the measurement of mass change with water absorption, UT-CTT shows relatively anti water absorption property due to characteristics of tapes laminates structure and high V_f.

(2) Influence of water absorption on flexural properties:
The flexural properties of both DCFRTP were found to be decreased by water absorption. Especially, decrease in shear modulus of the resin by water absorption contributes significantly to the decrease in the flexural modulus of DCFRTP. Furthermore, it can be assumed that the interfacial adhesion between chopped tapes is degraded due to the absorbed water and it leads to decrease in the flexural strength of UT-CTT.

(3) Temperature dependence of flexural properties:
It was found that the DCFRTP showed temperature dependence in flexural properties and it was attributed to characteristics of PA6. However, it cannot observed the effect of absorbed water which freezing. On the contrary, DCFRTP with water absorption at -30 degrees Celsius performed flexural properties which close to the dry condition at 21 degrees Celsius.

The temperature dependence in high temperature range is currently under investigation. Additionally, influences of water absorption on the mechanical properties of CPT with PP resin are also under investigation.

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