A Polymer Colloidal Technique for Enhancing Bending Properties of Carbon Fiber-Reinforced Thermoplastics Using Nylon Modifier

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Abstract

To enhance the bending properties of carbon fiber-reinforced thermoplastics (CFRTPs) by improving their interfacial properties, a new colloidal technique has been developed in this work. First, colloidal polymer containing the main components of thermoplastic nylon resin was synthesized from nylon powder and surfactants through emulsion polymerization and then adsorbed on the surface of carbon fibers by electrodeposition. The strength of the surface adhesion between the modified carbon fibers and nylon was estimated by measuring their interfacial shear strength (ISS) via fragmentation testing. The obtained results revealed that both the ISS and impregnation ratio of nylon depended on the amount and composition of the adsorbed particles. Furthermore, the relationship between the interfacial and bending properties of CFRTP was clarified. The results of three-point bending tests showed that the contribution of the impregnation ratio of nylon to the enhancement of the bending strength of CFRTP was much larger than that of ISS.

1. Introduction

Carbon fiber-reinforced plastics (CFRPs) are lightweight composites that can be used in construction materials, transporters, and sports equipment [1, 2]. However, they also exhibit low recyclability because their matrices are composed of thermosetting resins (such as epoxy resin) [3]. As a result, carbon fiber-reinforced thermoplastics (CFRTPs) that possess the ability to be remolded by heating have been developed because of their easy manufacture and high recyclability [4-6]. Generally, the mechanical properties of composite materials strongly depend on their interfacial properties [7], which were intensely studied in previous works (including those of the composites fabricated from epoxy resins) [8, 9].

For example, to enhance the surface adhesion between carbon fibers and the resin matrix of CFRTP, various techniques for the modification of the fiber surface with polymers or inorganic materials were developed [10-12]. When acrylic polymers were used for this purpose, the strength of interfacial adhesion was significantly improved through the copolymerization of methyl methacrylate with 2-hydroxyethyl acrylate [13]. Recently, colloidal poly(methyl methacrylate) (PMMA) has been synthesized through soap-free emulsion polymerization and then adsorbed on the surface of carbon fibers via electrodeposition [14] or electrostatic interactions [15, 16]. It was found that the adhesion strength between carbon fibers and PMMA resin increased with increasing

amount of the adsorbed particles because of the stronger interaction between these two phases. Additionally, the impregnation ratio of the resin increased because the composition of the adsorbed particles was identical to that of the matrix. In the present study, the effect of the interfacial properties of CFRTP (such as the surface adhesion strength or impregnation ratio of the resin) on its bending characteristics was investigated using nylon as the matrix resin.
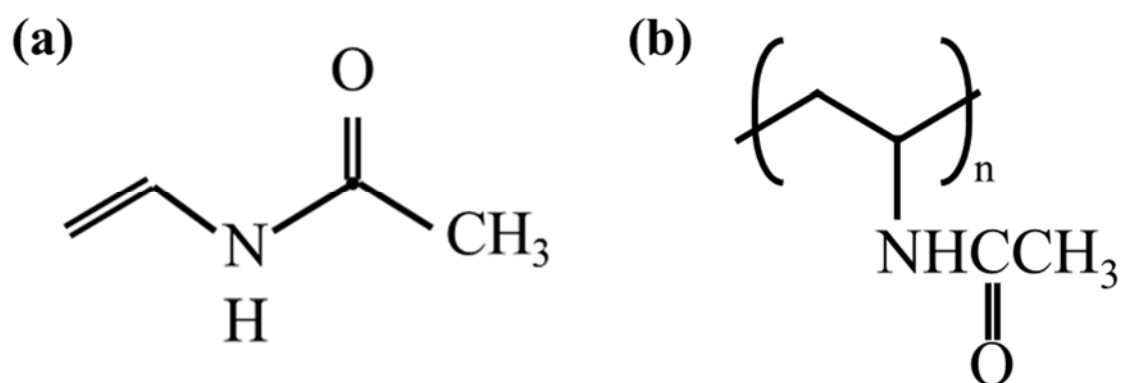
2. Experimental

2.1 Preparation of colloidal polymer dispersion

Nylon powder (PA12, TORAY) with an average particle diameter of 5 μm was dispersed in water using a surfactant (such as cetyltrimethylammonium bromide (CTAB, Tokyo Chemical Industry) or Span 20 (Tokyo Chemical Industry)) to obtain an aqueous dispersion of colloidal nylon-based polymer that could be easily adsorbed on the surface of carbon fibers (See Appendix). To decrease the average size of polymer particles, a soap-free emulsion polymerization procedure was performed [17]. The water used in the polymerization reaction was purified using a purification system (Auto Still WG250, Yamato) followed by bubbling with nitrogen gas to remove any dissolved oxygen species. Styrene monomer (Tokyo Chemical Industry) was washed with a 10 wt.%

sodium hydroxide (NACALAI TESQUE, INC) solution four times to remove

polymerization inhibitors and then purified by distillation under reduced pressure.

N-vinyl acetamide (NVA, SHOWA DENKO K.K.) reagent was used in the

polymerization reaction as received because it contained NH and CO functional groups,

which were also present in the nylon monomer (its chemical structure is shown in **Fig.**

1a). 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, Wako Pure

Chemical Industries) was used as an initiator without further purification [18].

The polymerization reaction was performed inside a round-bottom reactor with

a diameter of 30 mm. Both the temperature of the reactor and rotation speed of the

impeller were controlled by a magnetic stirrer equipped with a heater (RCH-20L,

EYELA) (the amounts of various reagents used for the polymerization reaction are

listed in **Table 1**). Based on the results of previous studies, the reaction time was set to 6

h because the polymerization process was mainly complete after this period [19, 20].

The polymerization procedure was performed as follows. Specific amounts of pure

water and the initiator (**Table 1**) were poured into the reactor followed by monomer

addition. After that, the reactor was sealed with a cap and heated to 70 °C using an

electric heater. The reaction mixture was agitated at a speed of 130 rpm using the

magnetic stirrer. The average size of the synthesized particles composed of polystyrene

cores and polyNVA shells (**Fig. 1b**) was 71.1 nm [19]. To determine the molecular

weights of polyNVA-polystyrene particles and the corresponding mass spectrometry

peaks, a matrix-assisted laser desorption ionization time-of-flight mass spectrometry

technique (MALDI-TOF-MS; AXINA-CFR+, SHIMADZU) was used. Polymer

samples were prepared using dithranol (Sigma-Aldrich) as a matrix followed by

freeze-drying (the details of the utilized preparation procedure are provided elsewhere

[21]).

(a)

(b)

Fig. 1. Chemical structures of (a) NVA and (b) polyNVA.

Table 1. Experimental parameters of the polymerization reaction.

Water [g]	150
Styrene [g]	5.0
NVA [g]	20.0
VA-044 [mg]	98.4
Temperature [°C]	70
Rotation speed of impeller [rpm]	130

2.2 Surface modification of carbon fibers with colloidal polymer thorough electrodeposition

Before use, carbon fibers (HTS40, Toho Tenax Co., LTD.) were treated with acetone to remove sizing agents. After that, they were immersed in the prepared colloidal polymer to allow polymer particles to adsorb on their surfaces using an electrodeposition system [14], in which the three thousands carbon fibers were attached to the electrode. To calculate the number of the particles adsorbed on the carbon fiber surface, a thermal gravimetric analyzer (TG, DTG-60AH, SHIMADZU) was used. During analysis, the sample was heated to 500 °C at a heating rate of 10 °C/min. The observed decrease in the sample weight corresponded to the amount of polymer particles adsorbed on the carbon fibers (m_1). The amount of particles per unit surface area of the carbon fiber (M) was calculated using the following equation [14, 15]:

$$M = \frac{\rho S m_1}{D \pi m_2} \qquad (1)$$

where D, m_2, and S were the average diameter, mass, and sectional area of carbon fibers, respectively.

2.3. Evaluation of CFRTP interfacial properties

To evaluate the interfacial shear strength (ISS) τ_m of a single carbon fiber,

fragmentation tests were performed under a microscope (MS-804, MORITEX

Corporation) using a tensile testing machine (10073B, JAPAN HIGH TECH Co, Ltd.).

Specimens for analysis were prepared as follows. First, a single carbon fiber

sandwiched between two nylon films (PA6, TORAY) was hot-pressed at a temperature

of 260 °C and pressures of 5 MPa and 40 MPa for 30 s and 1 min, respectively, using a

heater press (N4003-00, NPa system) and then quenched by placing the resulting film

between the two steel plates cooled with water to a temperature of 25 °C. After that, the

film was cut into strips with gauge lengths of 30 mm and widths of 2 mm. The testing

procedure was conducted until the completion of the fragmentation process (which

occurred at a tensile strain of about 15%), and the average length of the fragmented

carbon fibers <L> was measured. To characterize the interfacial properties of a single

carbon fiber, five samples were subjected to fragmentation testing. The ISS of the

interface between the carbon fibers and the resin was calculated via the following

equation [14]:

$$\tau_m = \frac{D\sigma_f}{2l_c} \qquad (2)$$

where the effective length (l_c) was defined as

$$<L> = \frac{3}{4}l_c \qquad (3)$$

The average diameter of carbon fibers was measured by reflecting a He-Ne laser beam

from their surface. The tensile strength of the carbon fibers (σ_f) with the length l_c was estimated by conducting the Weibull analysis of the results of single-fiber tensile tests [22]. The latter were performed using a tensile testing machine (SDW-1000SS-E-SL, IMADA SEISAKUSHO Co, Ltd.), which was operated at a gauge length of 25 mm and crosshead speed of 1 mm/min.

CFRTP cross-sections were examined by field emission scanning electron microcopy (FE-SEM, JSM-7500FA, JEOL). The corresponding specimens were prepared by embedding the photocurable resin (ARONIX, Toagosei Co., Ltd.) using a polishing machine (ML-150P, Maruto Instrument Co., Ltd.) and then coated with a thin osmium film by vapor deposition (Osmium Plasma Coater OPC60A, Filgen).

2.4. Evaluation of CFRTP bending properties

CFRTP samples were prepared as follows. The carbon fibers sandwiched between nylon films were hot-pressed a temperature of 260 °C and pressures of 0.3 MPa and 5 MPa for 3 min and 2 min, respectively, on the heater press (N4003-00, NPa system) followed by quenching between two steel plates cooled with water to 25 °C. The obtained prepregs were utilized to fabricate unidirectional CFRTP specimens by a prepreg-based hot pressing method at a temperature of 260 °C and pressures of 0.3 MPa

and 5 MPa for 5 min each [23, 24]. To estimate the amount of voids in the CFRTP

structure, two different volumes of the CFRTP specimens (V_{weight} and V_{cal}) based on

their weights and lengths, respectively, were determined [25]. V_{cal} represented the

difference between the total volume calculated from the dimensions of the CFRTP

specimens and the volume of the carbon fibers. The volume of the nylon resin in the

CFRTP samples V_{weight} was determined as a difference between the weights of the

carbon fibers and CFRTP divided by the density of the nylon film. The impregnation

ratio of the resin ϕ was defined as follows:

$$\phi = \frac{V_{weight}}{V_{cal}} \qquad (4)$$

Three-point bending tests were performed using the tensile testing machine

(SDW-1000SS-E-SL, IMADA SEISAKUSHO) to measure the CFRTP bending strength

σ. During measurements, specimens with a fiber content of 30 vol.%, which was

calculated from the masses of the carbon fibers and nylon films used for CFRTP

fabrication, were loaded at a crosshead speed of 5 mm/min. Bending strength was

calculated according to the following equation:

$$\sigma = \frac{3F_{max}L}{2wh^2} \qquad (5)$$

where F_{max} was the maximum load, L was the distance between the supporting points,

and w (100 mm) and h (2 mm) were the width and thickness of the CFRTP specimen,

respectively.

3. Results and discussion

3.1 Adsorption of colloidal polymer on carbon fibers and its influence on ISS

In this study, the electrodeposition technique was used to modify the surface of carbon fibers with a colloidal polymer. **Fig. 2** depicts the amount of particles adsorbed on the carbon fiber surface as a function of the concentration of nylon powder in the dispersion containing CTAB surfactant (during measurements, a voltage of 30 V was applied for 30 s). The obtained results show that the amount of adsorbed particles increased with increasing nylon concentration, suggesting that this parameter could be easily controlled by varying the concentration of polymer in the colloidal solution.

The influence of the amount of nylon particles adsorbed on the surface of carbon fibers on their surface properties (ISS and impregnation ratio) is described in **Fig. 3**. It shows that increasing the amount of adsorbed nylon particles increases both the ISS and impregnation ratio of nylon because of the stronger interactions between the nylon particles and the matrix (the obtained ISS data were in good agreement with the results of a previous study, in which PMMA was used as the matrix resin [14]). In particular,

the observed increase in the nylon impregnation ratio was mainly attributed to the

presence of nylon particles between carbon fibers.
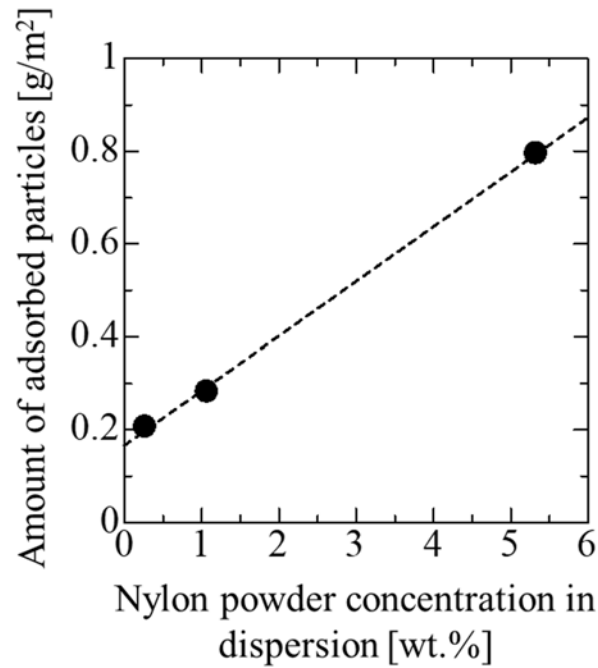
Fig. 2. Relative amount of nylon particles adsorbed on the surface of carbon fibers as a function of the nylon powder concentration in the dispersion containing CTAB surfactant.
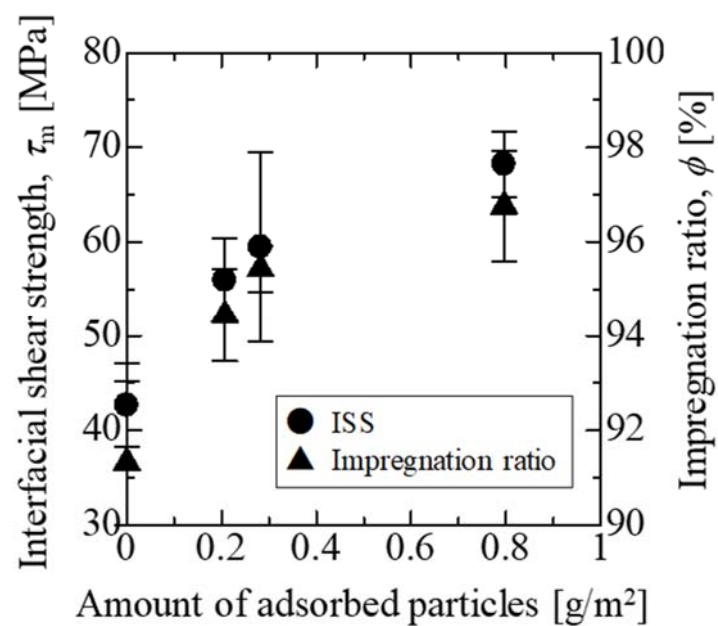
Fig. 3. Influence of the amount of nylon particles adsorbed on the surface of carbon fibers on their interfacial properties.

3.2 Influence of nylon impregnation ratio on the bending strength of CFRTP

The concentration of nylon powder in a colloidal suspension can produce a significant effect on the ISS of the resulting CFRTP specimen. Thus, the surface modification of carbon fibers with various colloidal polymers (including PA12 mixed with Span20 or CTAB and polyNVA-polystyrene particles) was performed. The obtained ISS values were very close, and the relationships between the impregnation ratios and bending strengths of the produced CFRTP specimens are shown in **Fig. 4**. The SEM image presented in **Fig. 5a** shows the existence of voids in the CFRTP structure with a low impregnation ratio, which decrease its bending strength. On the other hand, at $\phi = 97.7\%$ (**Fig. 5b**), the bending strength of CFRTP was noticeably higher. Hence, to enhance the bending properties of CFRTP, it is extremely important to prevent the formation of voids in its structure.
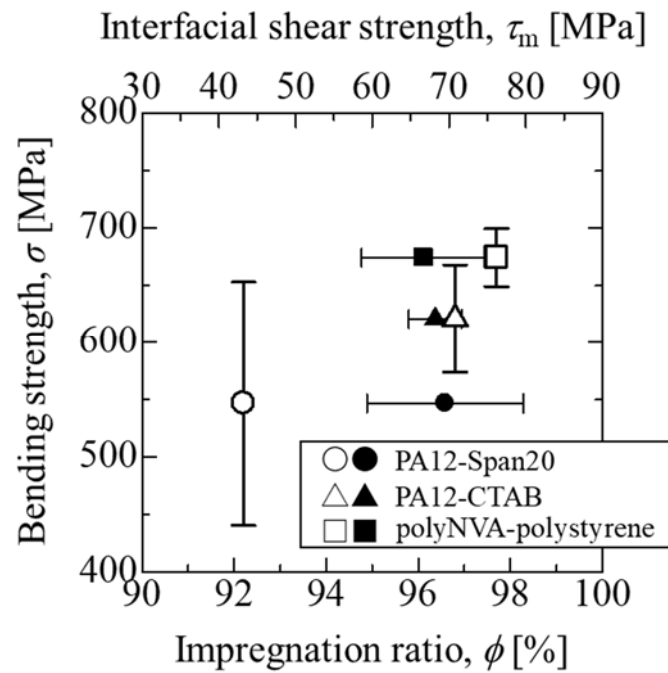
Fig. 4. Influence of the impregnation ratio of nylon resin (○△□) on the bending strength of CFRTP at close ISS values (●▲■).
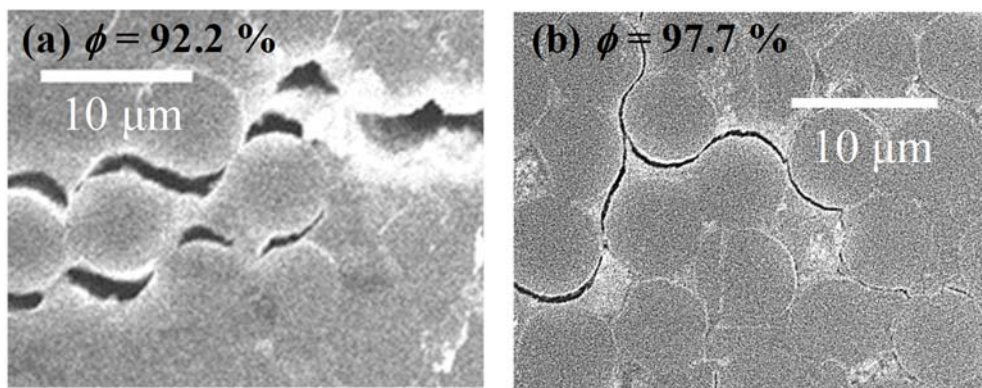

**Fig. 5. SEM images of the CFRTP cross-section obtained at (a) ϕ = 92.2% and (b) ϕ = 97.7%.**

3.3 Influence of ISS on the bending strength of CFRTP

In this section, the influence of ISS on the bending strength of CFRTP was investigated by performing three-point bending tests. To prepare CFRTP specimens

with the same impregnation ratios, three different types of polymer with various

initiator concentrations were synthesized through soap-free emulsion polymerization.

As shown in **Fig. 6**, increasing the initiator concentration decreased the molecular

weight of the produced polymer due to the increased number of terminal groups

contained by initiator molecules. **Fig. 7** shows the influence of the molecular weight of

the polyNVA-polystyrene particles adsorbed on the surface of carbon fibers on the

interfacial properties of CFRTP observed after applying a voltage of 30 V to the

electrodeposition system for 30 s. Because the sizes of the polyNVA-polystyrene

particles were small, their fractions adsorbed on the carbon fiber surface could not be

detected by thermal gravimetric analysis. As a result, very little effect of their molecular

weights on the amount of adsorbed particles was observed, and the impregnation ratio

of nylon remained virtually constant (as compared with the data presented in Fig. 3).

However, the difference in ISS obtained for different polymers was significant. Because

the strength of the intermolecular forces (especially hydrogen bonds) between the

polyNVA-polystyrene particles and the matrix resin increased with increasing

molecular weight [26], their interactions were enhanced. The produced particles were

covered with polyNVA species containing NH and CO functional groups [19], which

easily interacted with the nylon resin that possessed the same groups.
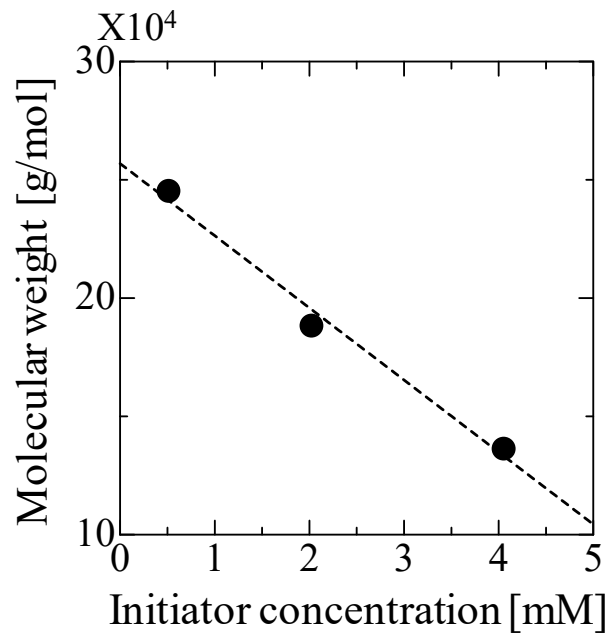
Fig. 6. Effect of the initiator concentration on the molecular weight of the synthesized polyNVA-polystyrene particles.
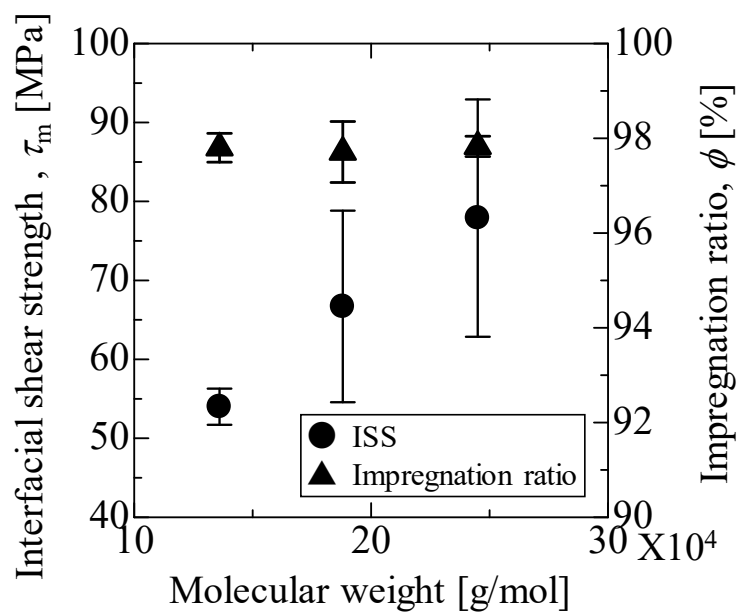

Fig. 7. Influence of the molecular weights of the polyNVA-polystyrene particles adsorbed on the surface of carbon fibers on the interfacial properties of the CFRTP specimens.

Thus, CFRTP samples with the same impregnation ratios and different ISS values were prepared to investigate the effect of ISS on their bending properties (see **Fig. 8**). The obtained results indicate that the bending strength of CFRTP was enhanced by the adsorption of polymer particles because of the increase in ISS at the interface between the carbon fibers and the nylon resin. After the test, interfacial peeling was not observed for the CFRTP specimens with higher ISS values, as shown in **Fig. 9a**. On the other hand, when the bending strength was relatively small, the CFRTP samples exhibited interfacial peeling after the bending test due to the low ISS magnitudes, as indicated by the white arrows depicted in **Fig. 9b**.

In this work, the effect of the surface modification of carbon fibers with colloidal polymers on the impregnation ratio of nylon and ISS was investigated. It was found that the influence of the nylon impregnation ratio on the bending strength of CFRTP was much greater than that of the ISS of the interface between the carbon fibers and nylon (see Figs. 4 and 8).
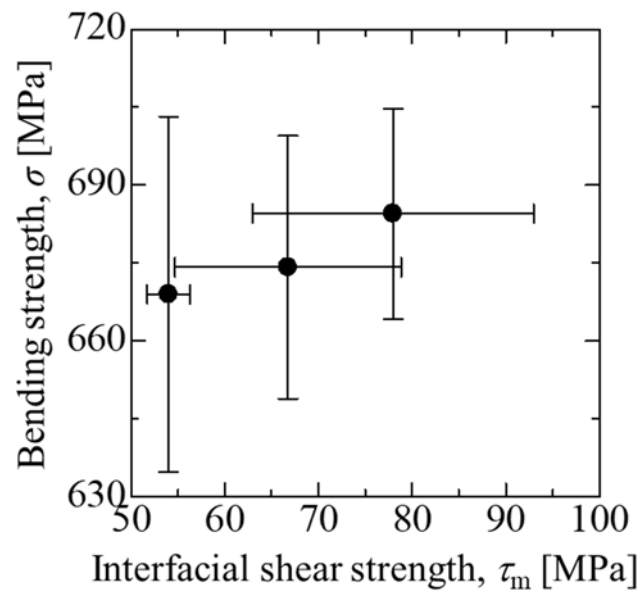
Fig. 8. Influence of ISS on the bending strength of CFRTP (the impregnation ratio of nylon remained almost constant).
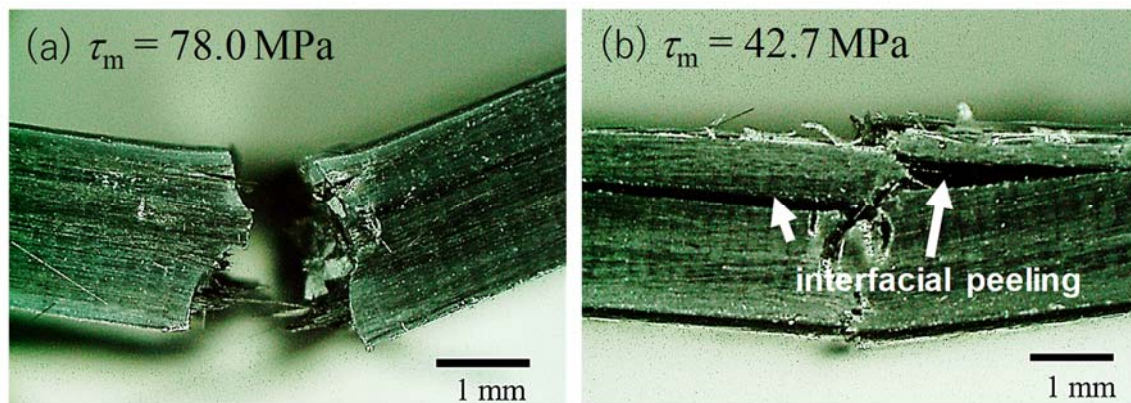
Fig. 9. CFRTP specimens with (a) τ_m = 78.0 MPa and (b) τ_m = 42.7 MPa after bending tests.

4. Conclusions

To enhance the bending properties of CFRTPs using nylon modifier, a special polymer colloidal technique was developed to improve the interfacial properties of carbon fibers. Nylon colloids were prepared using surfactants; polymer particles were

synthesized from NVA through soap-free emulsion polymerization; and the surface modification of carbon fibers with the colloidal polymer was conducted via electrodeposition. As a result, the effects of the impregnation ratio of nylon and ISS on the bending properties of CFRTPs were clarified, indicating that the contribution of the nylon impregnation ratio to its bending strength was much larger than that of ISS. Hence, the surface modification of carbon fibers with colloidal polymers can be used to enhance the mechanical performance of CFRTPs.

Appendix

To disperse 230 mg of nylon powder in 75 g of water, 400 mg of surfactant was added, and the resulting mixture was subjected to ultrasonic irradiation for 30 min to prepare the colloidal polymer.

Acknowledgements

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